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A Gold- and Brønsted acid Catalytic Interplay Towards the Synthesis of Highly Substituted Tetrahydrocarbazoles

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The reaction of indoles and stabilized cyclopropyl alkynes under gold- and/or gold & Brønsted acid-catalysis provided access to highly substituted tetrahydrocarbazoles. A mechanistic study revealed the complex mechanism underlying these processes and the opportunistic cooperation of Lewis and Brønsted acid-catalysts towards the formation of complex molecular scaffolds.

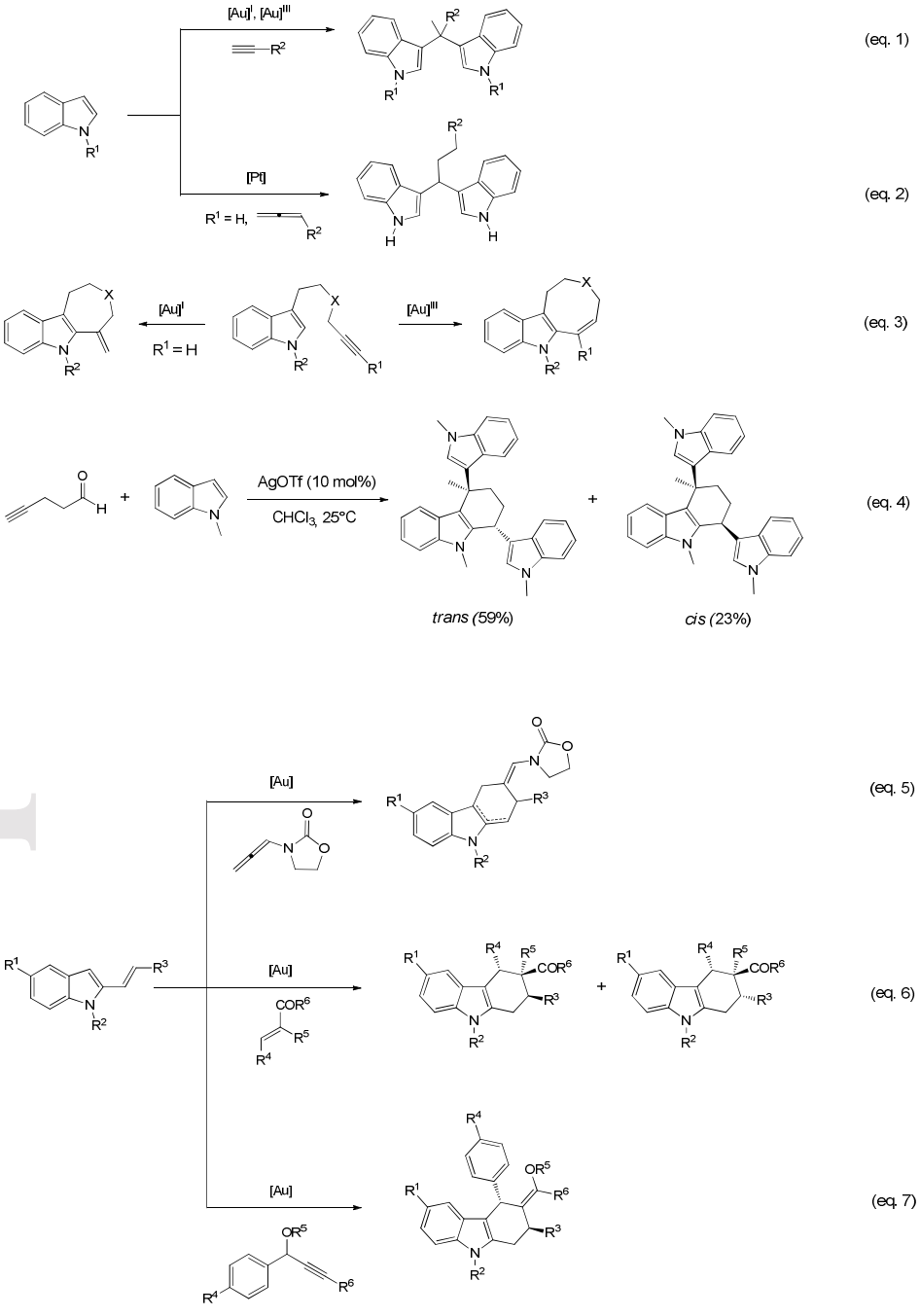
Keywords: Gold-catalysis • Cycloisomerization • Tetrahydrocarbazoles • Heterocycles • Brønsted Acid- catalysis

Introduction

Transition metal-catalyzed hydroarylations of C-C multiple bonds have attracted considerable attention as an efficient approach to functionalize arenes. The interest in this field has led to the development of a number of effective protocols for the hydroarylation of both alkenes[1,2] and alkynes.[2,3] Gold has played a preminent role in this context, acting as a Lewis acid to activate alkynes towards a variety of nucleophiles including arenes and heteroarenes among many others.[4] Indoles, being important motifs present in a large variety of bioactive molecules, have been already explored in these transformations. Thus, both *Echavarren*[5] and *He'*s groups[6] have developed methods where simple indoles react intermolecularly with terminal alkynes in the presence of cationic gold(I) and gold(III) complexes respectively, affording bisindolyl derivatives (Scheme 1, eq. 1). Allenes could also be used as reaction counterparts in the presence of a platinum catalyst (Scheme 1, eq. 2).[7] Intramolecular versions of these transformations have also been studied:[5] C3-substituted indoles react with alkynes in the presence of gold catalysts to give 7- and 8-membered rings in a process controlled by the oxidation state of the catalyst (Scheme 1, eq. 3). A highly efficient synthesis of substituted tetrahydrocarbazoles from pent-4-ynal and indoles using silver(I) catalysts

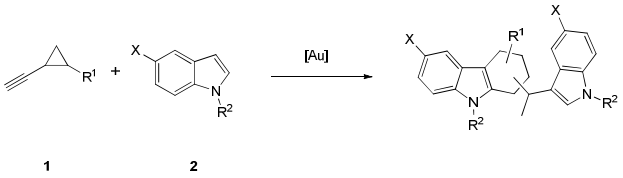
has also been recently reported (Scheme 1, eq. 4).[8] The formation of tetrahydrocarbazole derivatives via gold-catalyzed intermolecular cycloadditions between 2-vinylindoles and different dienophiles such as *N*-allenamides[9], conjugated esters[10] and propargylic esters has also been established (Scheme 1, eq. 5-7).[11] Additional developments in this field are granted given the presence of tetrahydrocarbazole blueprints in many natural products and pharmaceuticals.[12]

Scheme 1. Gold-, platinum- and silver-catalyzed synthesis of indolyl derivatives



Based on our going interest in the use of gold to streamline the synthesis of valuable building blocks via multicomponent reactions,[13] we decided to investigate the formation of highly substituted carbocycles using indoles **2** and stabilized cyclopropyl alkynes **1** as potential reaction partners (Scheme 2). Cyclopropyl rings are privileged motifs towards the construction of molecular complexity[14] and in combination with alkynes and gold catalysis can offer access to previously unknown molecular assemblies.[15]

Scheme 2. This work

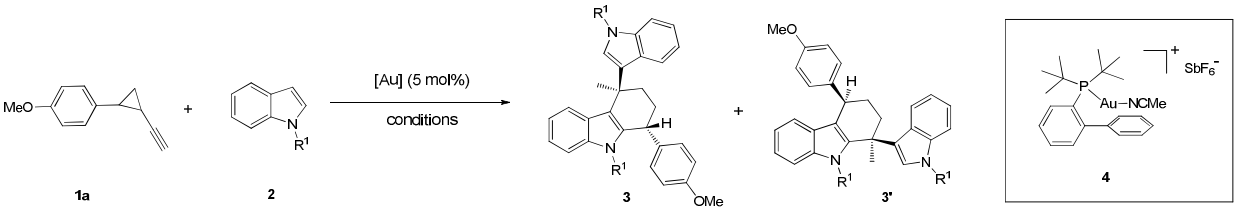


1 **2**

Results and Discussion

The reaction of 1-(2-ethynylcyclopropyl)-4-methoxybenzene (**1a**) with different *N*-protected indoles **2** in the presence of various gold catalysts was used to find the optimal conditions (Table 1). When **1a** was combined with *N*-benzyl protected indole (**2a**) no conversion or only traces of the desired products **3a** and **3'a** were observed using gold catalysts either bearing σ-donor such as IPr (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), Ph_3P ot $(t\text{Bu})_3P$, or π-acceptor (phosphite) ligands (Table 1, entries 1-5). The use of cationic gold complex **4**[16] in toluene, afforded complete conversion of the starting materials into tetrahydrocarbazoles **3a** and **3'a** (Table 1, entry 6). The reaction was regioselective favoring tetrahydrocarbazole **3a** over **3'a** in a 6:1 ratio. Both **3a** and **3'a** where isolated in high yield as an unseparable 2:1 mixture of diastereoisomers. The same conditions were applied to *N*-methyl indole (**2b**) which produced a 2:1 ratio of regioisomers **3b** and **3'b** in 60% yield (entry 7). Upon heating the reaction mixture to 80 ^{o}C a 4:1 regioisomeric mixture of the corresponding tetrahydrocarbazoles was obtained in 88% yield (entry 8). Having established cationic gold complex **4** as catalyst, we decided to apply these reaction conditions to non-protected indole (**2c**). Using **4** in toluene, dichloromethane and 1,2-dichloroethane as solvents, the reaction showed no conversion to products **3c** and **3'c** even after prolongued stirring and heating (entries 9-11). Reaction in dry THF at 100 ^{o}C afforded a 1:1 mixture of regioisomers **3c** and **3'c** which could be isolated in 92% yield (entry 12).

Table 1. Optimization of Reaction conditions.[a,b]

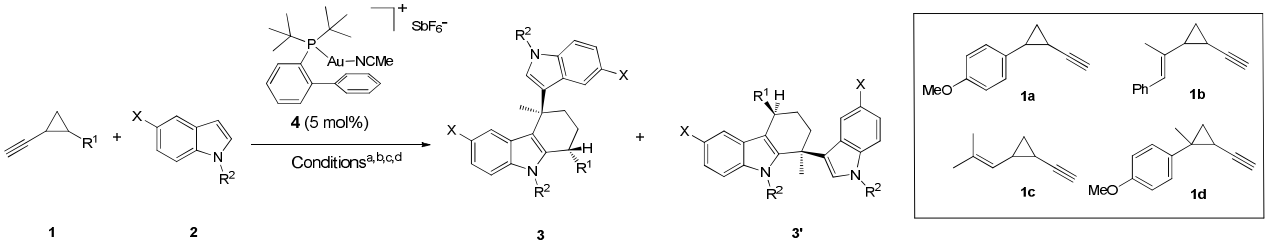


Entry	R^1	Conditions	Yield[c] / regioisomeric ratio 3:3' / (d. r.)[d]
1	Bn (**2a**)	IPrAuNTf$_2$,[e] CH_2Cl_2, 25°C, 48 h	No reaction
2	Bn (**2a**)	$Ph_3PAuNTf_2$, CH_2Cl_2, 25°C, 48 h	Traces
3	Bn (**2a**)	(*t*-Bu)$_3$PAuNTf$_2$, CH_2Cl_2, 25°C, 48 h	Traces
4	Bn (**2a**)	$(PhO)_3PAuSbF_6$, CH_2Cl_2, 25°C, 3 h	Traces
5	Bn (**2a**)	$(PhO)_3PAuSbF_6$, CH_2Cl_2, 50°C, 72 h	Traces
6	Bn (**2a**)	**4**,Toluene, 25°C, 24 h	95 / 6:1 / (2:1)
7	Me (**2b**)	**4**,Toluene, 25°C, 24 h	60 / 2:1 / (2:1)
8	Me (**2b**)	**4**,Toluene, 80°C, 12 h	88 / 4:1 / (2:1)
9	H (**2c**)	**4**, Toluene, 25°C, 24 h	No reaction
10	H (**2c**)	**4**, CH_2Cl_2, 25°C, 24 h	No reaction
11	H (**2c**)	**4**, 1,2-$C_2H_4Cl_2$, 80°C, 24 h	No reaction
12	H (**2c**)	**4**,THF, 100°C, 12 h	92 / 1:1 / (1:1)

[a] Reaction [0.1M]. [b] Major diastereoisomer depicted. [c] Isolated yield after column chromatography. [d] d.r.: diastereomeric ratio measured in the crude ^{1}H-NMR for both major (**3**) and minor (**3'**) regioisomers. [e] IPr: 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene.

With the best conditions in hand, using catalyst **4** in toluene at 80°C for *N*-protected indoles and THF at 100 °C for non-protected ones, we then set out to explore the scope of this transformation (Table 2). The reaction tolerates different groups at the nitrogen atom as well as at the C5-position of the indole counterpart, thus yielding the corresponding tetrahydrocarbazoles **3a-b/3'a-b**, **3d-m/3'd-m** in 42-95% with regioselectivities up to 10:1 (entries 1-12). The scope of the reaction was expanded to different cyclopropyl alkynes bearing substituents able to stabilize the positive electron density developed during the cyclopropyl-ring-opening process. Alkynes **1b-1d** reacted with *N*-benzyl or *N*-methyl indoles affording products **3n-p/3'n-p** and **3q-r/3'q-r** respectively (entries 13-17). An additional substituent at position 2 of the cyclopropyl ring was also tolerated (**1d**) affording the desired products **3s-t/3's-t** in good yields (entries 18-19). In these cases, the tetrahydrocarbazoles were obtained as 5:1 to 1:1 mixtures of diastereoisomers under the standard reaction conditions. Noticing the variability of diastereomeric mixtures observed throughout these series, we then decided to run the reaction in the presence of base in order to check its influence in the selectivity of the process (Table 2, last column). Recently, examples of Brønsted acid catalysis initially assigned to gold organometallic catalysis have been reported.[17] Remarkably, in all cases, the ratio between the regioisomers **3** and **3'** improved by the addition of 0.5 or 1.0 equivalents of $NaHCO_3$. However, no change in the diastereoselectivity of the reaction was observed.

Table 2. Scope of gold-catalyzed cycloisomerization of 1-cyclopropyl-alkynes.



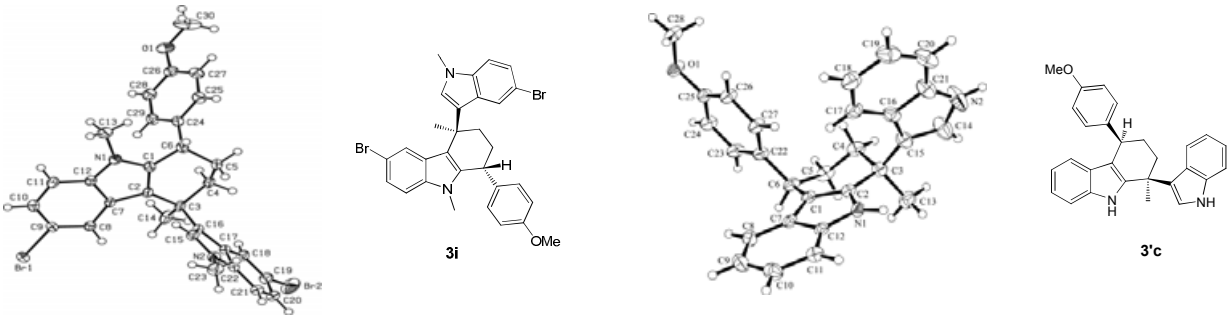
Entry	Alkyne	X	R^1	Product	Yield[e] / regioisomeric ratio 3:3' / (d. r.) No base	Yield[e] / regioisomeric ratio 3:3' / (d. r.) Base
1	**1a**	H	Bn (**2a**)	**3a**	95 / 6:1[a] / (2:1)	83 / 12:1[c] / (2:1)
2	**1a**	H	Me (**2b**)	**3b**	88 / 4:1[a] / (2:1)	74 / 6:1[d] / (2:1)
3	**1a**	H	PMB[f] (**2d**)	**3d**	76 / 7:1[a] / (2:1)	63 / 7:1[c] / (2:1)
4	**1a**	H	Cynnamyl (**2e**)	**3e**	78 / 10:1[a] (2:1)	-
5	**1a**	H	C_5H_{11} (**2f**)	**3f**	79 / 6:1[a] / (2:1)	75 / 6:1[d] / (2:1)
6	**1a**	OMe	Me (**2g**)	**3g**	86 / 2:1[a] / (2:1)	54 / 2:1[d] / (2:1)
7	**1a**	OMe	Bn (**2h**)	**3h**	56 / 3:1[a] / (2:1)	60 / 3:1[c] / (2:1)
8	**1a**	Br	Me (**2i**)	**3i**	72 / 8:1[a] / (2:1)	73 / 8:1[d] / (2:1)
9	**1a**	Br	Bn (**2j**)	**3j**	68 / 5:1[a] / (2:1)	76 / 7:1[c] / (2:1)
10	**1a**	Me	Me (**2k**)	**3k**	84 / 5:1[a] / (2:1)	77 / 7:1[d] / (2:1)
11	**1a**	Me	Bn (**2l**)	**3l**	42 / 3.5:1[a] / (2:1)	45 / 5:1[c] / (2:1)
12	**1a**	CN	Me (**2m**)	**3m**	52 / 2:1[a] / (2:1)	45 / 5:1[d] / (2:1)
13	**1b**	H	Bn (**2a**)	**3n**	81 / 5:1[a] / (1:1)	70 / 5:1[c] / (1:1)
14	**1b**	CN	Me (**2m**)	**3o**	79 / 7:1[a] / (5:1)	34 / 7:1[d] / (5:1)
15	**1b**	Br	Me (**2i**)	**3p**	82 / 5:1[a] / (1:1)	80 / 12:1[d] / (1:1)
16	**1c**	H	Bn (**2a**)	**3q**	57 / 5:1[a] / (1:1)	-
17	**1c**	Br	Me (**2i**)	**3r**	69 / 5:1[a] / (1:1)	-
18	**1d**	H	Bn (**2a**)	**3s**	63 / 5:1[a] / (1:1)	70 / 8:1[c] / (1:1)
19	**1d**	H	Me (**2b**)	**3t**	63 / 5:1[a] / (1:1)	56 / 6:1[d] / (1:1)
20	**1a**	H	H (**2c**)	**3c**	92 / 1:1[b] / (1:1)	-

21	**1a**	Br	H (**2n**)	**3u**	71 / 1:1[b] / (1:1)	-
22	**1a**	Me	H (**2o**)	**3v**	86 / 1:1[b] (1:1)	-
23	**1a**	CN	H (**2p**)	**3w**	68 / 1:1[b] / (1:1)	-

[a] Reaction conditions: Toluene [0.1M], **4** (5 mol%), 80°C, 12 h. [b] Reaction conditions: THF [0.1M], **4** (5 mol%), 100°C, 12 h. [c] Reaction conditions: Toluene [0.1M], **4** (5 mol%), $NaHCO_3$ (1.0 eq.), 80°C, 12 h. [d] Reaction conditions: Toluene [0.1M], **4** (5 mol%), $NaHCO_3$ (0.5 eq.), 80°C, 12 h. [e]Isolated yield after column chromatography. [f] PMB: 4-methoxybenzyl ether.

The scope of the reaction was further expanded to NH indoles (**2c**, **2n-p**). In sharp contrast to the reaction of *N*-protected indoles, these transformations proved not to be regioselective affording a 1:1 mixture of the corresponding tetrahydrocarbazoles **3c,u-w** and their regioisomers **3'c,u-w** (Table 2, entries 20-23). The structure of the major (**3**) and minor (**3'**) regioisomer was confirmed by X-Ray diffraction analysis on compounds **3i** and **3'c** respectively (Figure 1).

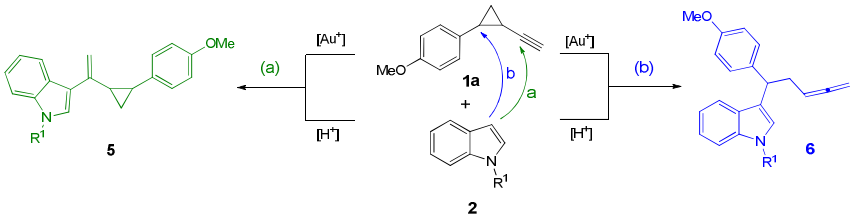
Figure 1. X-Ray diffraction analysis of compounds **3i** and **3'c**.[a]



[a] CCDC 1495025-1495026 contain the supplementary crystallographic data for this work. These data can be obtained free of charge from *The Cambridge Crystallographic Data Center* via www.ccdc.cam.ac.uk/data_request/cif.

Once the reaction scope had been established, we turned our attention to the underlying mechanism in these transformations. A likely scenario was envisioned involving the nucleophilic attack of indole **2** onto the gold- or Brønsted acid-activated cyclopropyl alkyne. Two distinct pathways would then arise depending on the regioselectivity of the nucleophilic attack of the indole counterpart. Intermediate **5** would be formed as a result of the attack onto the internal position of the alkyne (Scheme 3a, left) whereas allene intermediate **6** would arise by reaction onto the 2 position of the cyclopropyl ring (Scheme 3b, right).

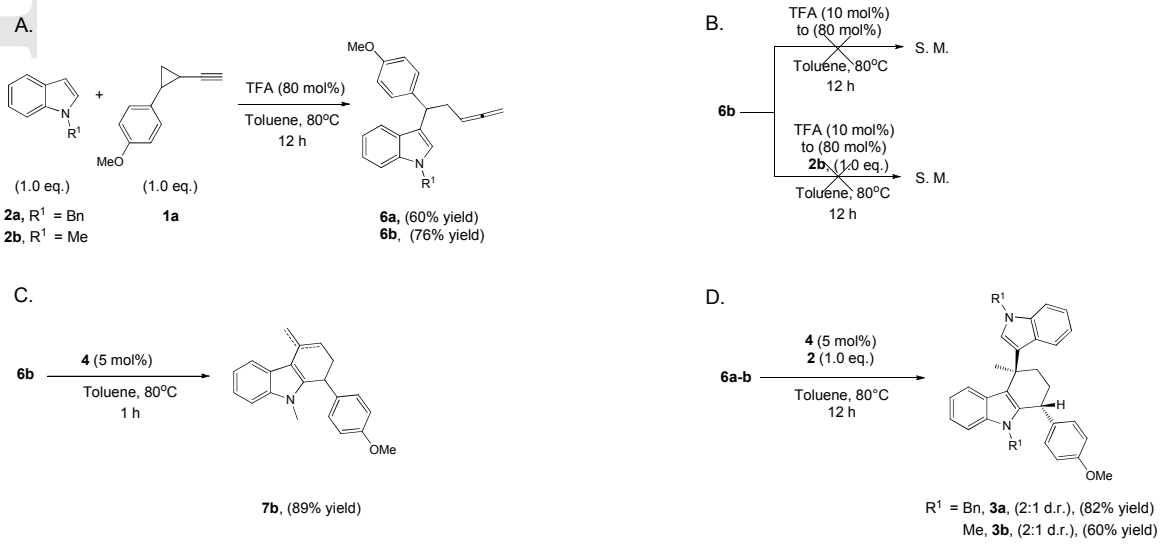
Scheme 3. Regioselective synthesis of **5** and **6**.



Control experiments were designed taking into account the possibility of both a gold- or a Brønsted-acid-catalysis (Scheme 4). First, the reaction between **1a** and *N*-benzyl or *N*-methyl indole **2a-b** was performed in the presence of different amounts of protic acids. Using catalytic amounts of trifluoroacetic acid (TFA, 10 mol%) allene **6** was detected although no total conversion could be achieved despite of prolonged heating (data not shown). In contrast, the reaction with substoichiometric amounts of TFA (80 mol%) afforded allenes **6a-b** in good yields (Scheme 4A). These reactions do not evolve into the tetrahydrocarbazoles products, confirming that the overall transformations cannot be fully Brønsted-acid-catalyzed processes. To confirm this hypothesis isolated allene **6b** was exposed to acidic conditions. In the presence of catalytic (10 mol%) and substoichiometric (80 mol%) amounts of TFA no conversion was observed, even in the presence of 1 equivalent of methyl indole **2b** (Scheme 4B). In contrast, the reaction of **6b** in the presence of 5 mol% of gold catalyst **4** (Scheme 4C) afforded total conversion to carbazole **7b** as a 2:1 regioisomeric mixture of *exo* and *endo* alkenes after one hour of reaction.

The fact that **7b** cannot be formed by protic acid confirms that the gold catalyst is indeed needed in these transformations.[5,6] Interestingly, the reaction of the allenyl intermediates **6a-b** in presence of one equivalent of the corresponding indoles **2a-b** and the gold catalyst **4** afforded tetrahydrocarbazoles **3a** and **3b** as single regioisomers in 60% to 82% yield as a 2:1 mixture of diastereoisomers (Scheme 4D).

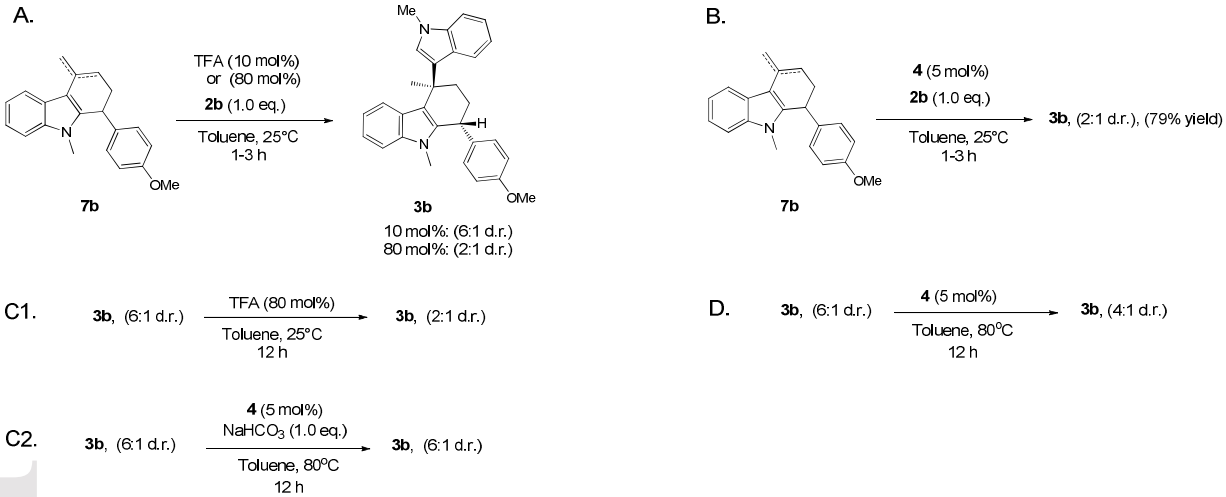
Scheme 4. Acid-catalyzed synthesis of allenes **6a-b** and gold-catalyzed formation of **7b** and **3a-b**.[a]



[a] HCl and *p*-TsOH were also used.

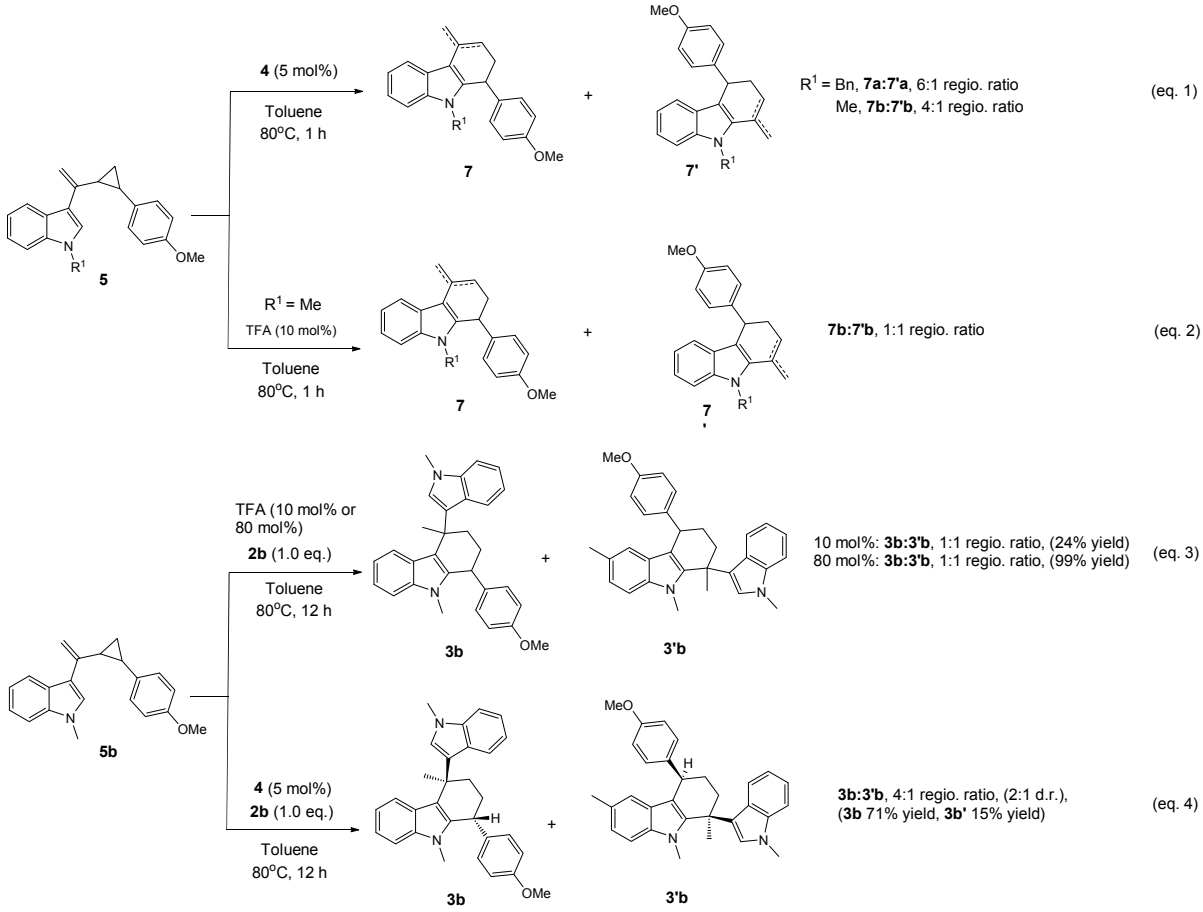
The ability of carbazole **7** to produce tetrahydrocarbazoles **3** was investigated next (Scheme 5). First, the reaction of **7b** in the presence of 10 and 80 mol% of TFA and one equivalent of methyl indole (**2b**) delivered the corresponding tetrahydrocarbazole **3b** as single regioisomer in 6:1 and 2:1 diastereomeric ratios, respectively (Scheme 5A). In contrast, the reaction in the presence of catalytic amounts of gold complex **4** afforded **3b** in 79% yield in a 2:1 diastereomeric ratio (Scheme 5B). The discrepancy with previous results, where final products were usually obtained as 2:1 diastereomeric mixtures (Table 2), prompted us to think about the possibility of acid- or gold-catalyzed epimerization reaction at the benzylic position of the products. To validate this hypothesis, a 6:1 diastereomeric mixture of the tetrahydrocarbazole **3b** was treated with 80 mol% of acid (Scheme 5C1). After 12 hours at room temperature, epimerization at the benzylic position of the tetrahydrocarbazole **3b** was observed affording a 2:1 diastereomeric mixture. Gold was also able to epimerize the benzylic position of **3b** (Scheme 5C2) from a diastereomeric ratio of 6:1 to 4:1. However, when 1 equivalent of $NaHCO_3$ was used (Scheme 5D) no epimerization was observed, thus confirming that acid is needed to promote the corresponding isomerization at the benzylic position.

Scheme 5. Acid- and gold-catalyzed synthesis of tetrahydrocarbazole **3b** and epimerization experiments.



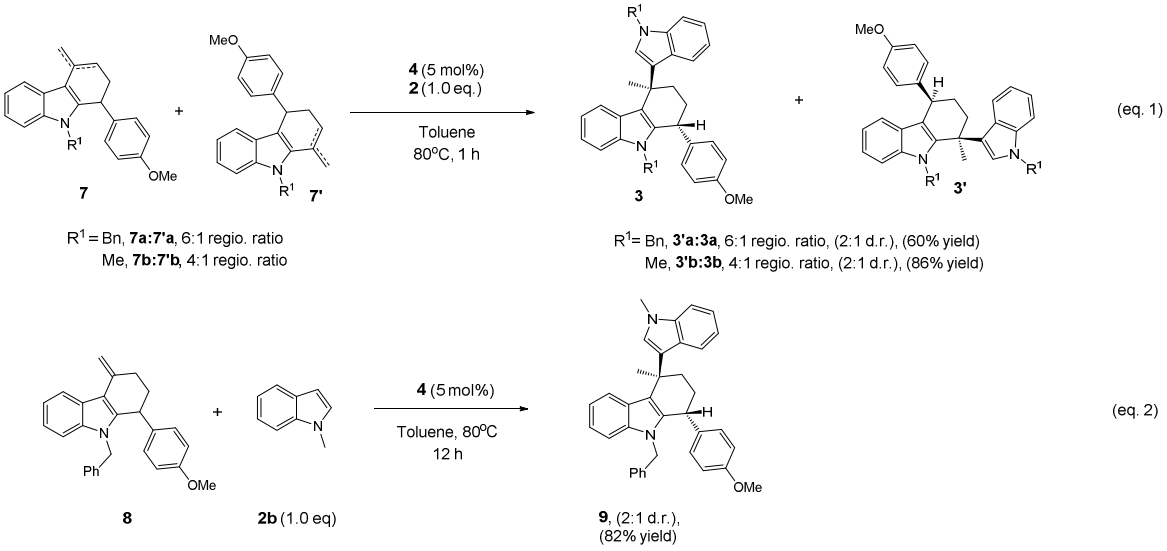
As shown in Scheme 4, experiments with allene **6** in presence of acid and gold catalyst **4** could not explain the formation of the observed minor regioisomer **3'**. Thus, we hypothesized that **3'** could be formed as a result of the direct attack of the indole to the alkyne moiety via vinyl cyclopropyl intermediate **5** (Scheme 3). **5** was synthetized independently and submitted to both gold and Brønsted acid catalysis (Scheme 6). The reaction with 5 mol% of **4** afforded different regioisomeric mixtures of carbazoles **7** and **7'** (Scheme 6, eq. 1). On the other hand, the reaction of **5b** in the presence of catalytic amounts of TFA afforded a 1:1 mixture of carbazoles **7b** and **7'b** (Scheme 6, eq. 2). Intermediate **5b** was also exposed to catalytic (10 mol%) and substoichiometric amounts (80 mol%) of TFA in the presence of indole **2b**, affording in both cases a 1:1 regioisomeric mixture of tetrahydrocarbazoles **3b** and **3'b** (Scheme 6, eq. 3). Interestingly, the reaction of **5b** in the presence of 5 mol% of the gold catalyst **4** afforded a 4:1 regioisomeric mixture of **3b** and **3'b** which could be isolated in 71 and 15% yields, respectively (Scheme 6, eq. 4).

Scheme 6. Reactivity of intermediate **5**.



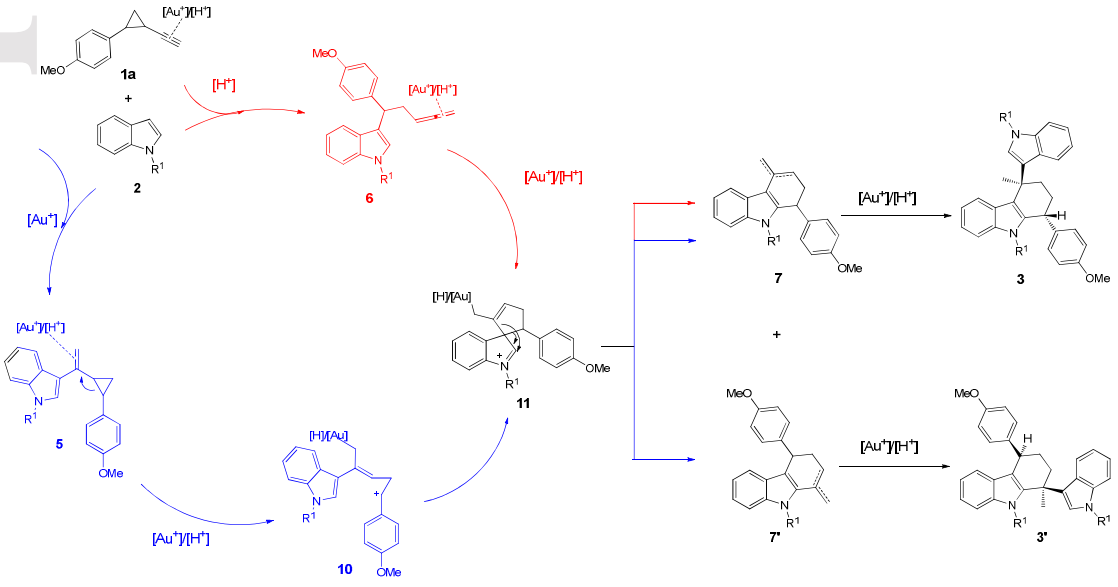
The formation of tetrahydrocarbazoles **3b** and **3'b** described in Scheme 6 can thus be explained via carbazoles **7** and **7'** respectively. For this reason one last set of experiments was designed in order to study this final step. A 6:1 regioisomeric mixture of intermediates **7a** and **7'a** was reacted with one equivalent of benzyl indole **2a** in the presence of catalytic amounts of gold catalyst **4** (Scheme 7). The reaction afforded a 6:1 regioisomeric mixture of the desired products **3a** and **3'a**. The same regioselective pattern was observed for intermediates **7b** and **7'b**, which provided a 4:1 regioisomeric mixture of **3b** and **3'b** (Scheme 7, eq. 1). The selectivity observed in this transformation as well as the regioselectivity observed in the formation of intermediates **7b** and **7'b** (Scheme 6) is in agreement with the results observed for the reaction between methyl indole and the corresponding alkyne **1a** under the standard reactions conditions (Table 1, entry 8). Moreover, the reaction of intermediate **8** in presence of one equivalent of methyl indole afforded the tetrahydrocabazol **9** in 82% yield as a single regioisomer (Scheme 7, eq. 2).

Scheme 7. Gold-catalyzed synthesis of products **3/3'** from intermediates **7/7'**.



A complete mechanistic picture[18] involving three main steps can be formulated using the collected data (Scheme 8). First, both gold and acid can catalyze the formation of intermediates **5** and **6** in a regio-divergent process. Gold-coordination to alkyne **1a** triggers the nucleophilic attack of indole **2** delivering vinyl cyclopropyl intermediate **5** (Scheme 8, blue). **5** can then be activated in the presence of both gold and/or acid triggering a cyclopropyl-ring opening to form 1,5-dipole **10**, which cyclizes to afford the spirocyclic intermediate **11**.[19] A subsequent ring expansion delivers regioisomeric mixtures of carbazoles **7** and **7'**. Further gold- or protic acid-activation of the double bond in **7** and **7'** followed by nucleophilic attack of a second molecule of indole afford the corresponding tetrahydrocarbazoles **3** and **3'**. Alternatively, Brønsted acid can activate the alkyne triggering the nucleophilic attack of the indole onto C2 of the cyclopropyl ring to produce allene **6** (Scheme 8, red). Then, after gold activation of the allene **6**, the intramolecular attack of the indole delivers spirocyclic intermediate **11**,[19] which selectively isomerizes to form **7** first, and regioisomer **3** thereafter.

Scheme 8. Mechanistic proposal.



Conclusions

This work describes the reactivity of 1-ethynylcyclopropyl derivates and indoles under gold catalysis. Highly substituted tetrahydrocarbazoles were obtained in good yields. The regioselectivity of the process is significant for *N*-protected indoles and can be improved in the presence of stoichiometric amounts of base. We have proposed that traces of acid produced in situ in the reaction mixture play a critical role in the selectivity of the cycloisomerization of the spyrocyclic intermediates to form the corresponding tetrahydrocarbazole products. We also demonstrated that the formation of the tetrahydrocarbazole products can be explained *via* gold-catalysis and/or *via* combination of gold- and protic acid-catalysis. A plausible reaction mechanism, where both gold and acid are involved, seem to be signalized by different control experiments performed, thus highlighting the mechanistic diversity of gold catalyzed reaction and the hitherto possibility of coexisting reaction pathways towards the observed reaction outcomes.

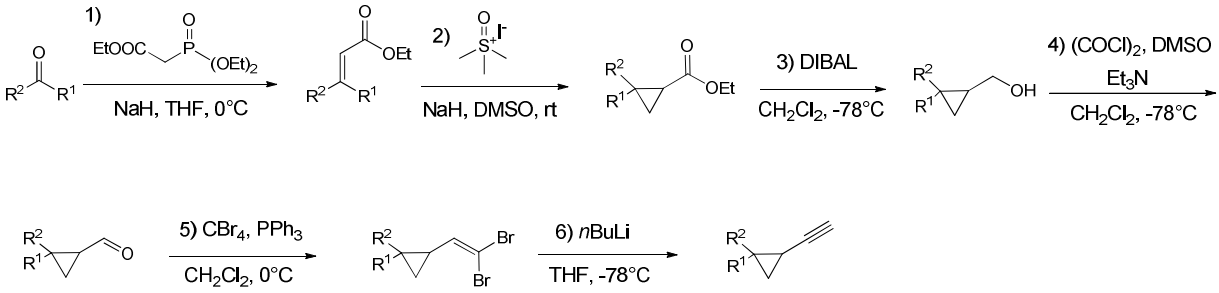
Experimental Section

General Informations

All reactions were carried under non-inert atmosphere. All reagents were used as received unless otherwise noted. Solvents were purchased in HPLC quality, degassed by purging thoroughly with nitrogen and dried over activated molecular sieves of appropriate size. Alternatively, they were purged with argon and passed through alumina columns in a solvent purification system (Innovative Technology). Reactions were monitored by thin layer chromatography (TLC) using Merck TLC silica gel 60 F_{254}. Flash column chromatography was performed over silacycle silica gel (230-400 mesh). NMR spectra were recorded on AV2 400 or AV2 500 MHz Bruker spectrometers. Chemical shifts are given in ppm. The spectra are calibrated to the residual 1H and 13C signals of the solvents. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet-doublet (dd), doublet-doublet-doublet (ddd), quintet (quint), septet (sept), multiplet (m), and broad (br). Infrared spectra were recorded on a JASCO FT/IR-4100 spectrometer. High-resolution electrospray ionization mass spectrometry was performed on a Finnigan MAT 900 (Thermo Finnigan, San Jose, CA; USA) doublefocusing magnetic sector mass spectrometer 10 spectra were acquired. A mass accuracy ≤ 2 ppm was obtained in the peak matching acquisition mode by using a solution containing 2 <l PEG200, 2 <l PPG450, and 1.5 mg NaOAc (all obtained from Sigma-Aldrich, CH-Buchs) dissolved in 100ml MeOH (HPLC Supra grade, Scharlau, E-Barcelona) as internal standard.

The separation of regioisomers 3/3‘ was not always possible. Regioisomeric and diastereoisomeric ratios have been calculated from the crude ^{1}H NMR mixture and the individual analytical data are described herein only when the isolation was possible.

Experimental procedure for the preparation of cyclopropyl alkynes ***1a-1d***



1) To a solution of NaH (1.05 eq.) in THF (0.8 M) at 0°C, triethyl phosphonoacetate (1.1 eq.) was added dropwise. The mixture was stirred at 0°C for 20 minutes. Then, the carbonyl compound (1.0 eq.) was added dropwise at 0°C. The reaction was stirred at 25°C for 12 hours and quenched with brine. Approximately 2/3 of the solvent was evaporated under reduced pressure. The aqueous layer was extracted with CH_2Cl_2 (2 times) and the combined organic layers were dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (pentane) to give the corresponding *α,β*-unsaturated ester in 82-95% yield.

2) To a solution of NaH (1.05 eq.) in THF (0.6 M) at 25°C, trimethylsulfoxonium iodine (1.15 eq.) was added as a solid in small portions. The mixture was stirred for 1 hour before a solution of the corresponding ester (1.0 eq.) in DMSO (1.0 M) was added. The mixture was stirred at room temperature for 12 hours. The reaction was quenched with brine and extracted with diethyl ether (3 times). The organic layers were dried over Na_2SO_4. Solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (pentane) to give the corresponding cyclopropyl ester in 62-90% yield.

3) To a solution of the corresponding cyclopropyl ester (1.0 eq.) in CH_2Cl_2 (0.2 M) at -78°C, DIBAL (1.0 M in hexane, 2.2 eq.) was added dropwise. The reaction was stirred at -78°C for 1 hour. The reaction was quenched with ethyl acetate (3 eq.) and diluted with diethyl ether. A saturated solution of Na/K-tartrate was added to the mixture and the reaction was stirred for another 3 hours till clear separation of the two phases was observed. The aqueous layer was extracted with diethyl ether and the combined organic layers were dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (hexane:ethyl acetate 4:1) to give the corresponding alcohol in 60-90% yield.

4) To a solution of oxalyl chloride (1.5 eq.) in CH_2Cl_2 (0.4 M), DMSO (2.3 eq.) was added dropwise. The reaction was stirred at -78°C for 1 hour. Then, the corresponding alcohol (1.0 eq.) was added dropwise in CH_2Cl_2 (1.4 M). The reaction was stirred at -78°C for 1 hour, and triethylamine (5.0 eq.) was added dropwise. The reaction was stirred at -78°C for another hour. The mixture was then warmed up to room temperature for another 30 minutes and quenched with a saturated solution of ammonium chloride. The aqueous layer was extracted with CH_2Cl_2 and the combined organic layers were dried over Na_2SO_4. The solvent was evaporated under reduced pressure. The crude product was used in the next step without further purification.

5) To a solution of CBr_4 (2.2 eq.) in CH_2Cl_2 (1.5 M) at 0°C, a solution of triphenylphosphine (4.4 eq.) in CH_2Cl_2 (1.5 M) was added dropwise. The resulting dark orange solution was stirred for 5 minutes. A solution of the corresponding cyclopropylaldehyde (1.0 eq.) dissolved in CH_2Cl_2 (1.0 M) was added dropwise. The solution was stirred at 0°C for 2-3 hours. The reaction mixture was quenched by addition of water. The aqueous layers where extracted with CH_2Cl_2. The combined organic layers were washed with water and brine. The organic layer was dried over $MgSO_4$ and the crude was purified by column chromatography on silica gel (hexane) to yield the dibromo derivatives in 65-80% yield.

6) To a solution of the corresponding cyclopropyl-dibromo derivate (1.0 eq.) in THF (0.2 M) at -78°C, *n*BuLi (1.0 M in hexane, 2.0 eq.) was added dropwise. The solution was stirred at -78°C for 3 hours and then warmed up to room temperature for 20 minutes. The resulting solution was cooled down to -78°C and water (1.05 eq.) was added dropwise. The reaction was stirred at room temperature for 12 hours. Water was added and the aqueous layer was extracted with EtOAc. The organic layers were dried over Na_2SO_4 and the crude was purified by column chromatography on silica gel (Hexane:EtOAc 25:1) to give the corresponding propargyl alcohol in 33-93% yield.

Analytical data for representative cyclopropyl alkynes

1-(2-Ethynylcyclopropyl)-4-methoxybenzene ***1a***

IR (neat, v/cm^{-1}): 3290, 3004, 2937, 2832, 1612, 1515, 1463, 1288, 1246, 1180, 1034, 827, 806, 674, 569; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.06-6.94 (m, 2H), 6.84-6.78 (m, 2H), 3.78 (s, 3H), 2.24 (ddd, *J* = 8.8, 6.1 Hz, 1H), 1.89 (d, *J* = 2.1 Hz, 1H), 1.47-1.37 (m, 1H), 1.31-1.24 (m, 1H), 1.22-1.12 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.4, 132.6, 127.3, 114.0, 86.6, 64.7, 55.4, 25.6, 17.1, 10.5 ppm; HRMS (ESI): m/z: calcd for $C_{12}H_{13}O^+$: 173.09609, found: 173.09627.

(2-(2-Ethynylcyclopropyl)prop-1-en-1-yl)benzene ***1b***

IR (neat, v/cm^{-1}): 2970, 1738, 1513, 1439, 1375, 1231, 1240, 1066, 1054, 894, 834, 696, 667, 571; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (t, *J* = 7.6 Hz, 2H), 7.24-7.14 (m, 3H), 6.35 (s, 1H), 1.93 (dt, *J* = 8.7, 5.7 Hz, 1H), 1.88 (d, *J* = 2.0 Hz, 1H), 1.77 (s, 3H), 1.42 (tdt, *J* = 6.9, 5.1, 1.9 Hz, 1H), 1.19-1.00 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0, 136.4, 128.97, 128.96, 128.2, 126.3, 125.4, 86.8, 64.6, 30.7, 15.8, 14.5, 7.1 ppm; HRMS (EI): m/z: calcd for $C_{14}H_{14}^+$: 182.10955, found: 182.10689.

1-(2-Ethynyl-1-methylcyclopropyl)-4-methoxybenzene ***1d***

IR (neat, v/cm^{-1}): 3291, 2113, 1702, 1643, 1598, 1492, 1443, 1378, 1223, 1202, 1173, 1119, 1074, 1056, 1029, 953, 942, 918, 844, 780, 739, 698, 648, 600, 508, 492; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22-7.17 (m, 2H), 6.85-6.80 (m, 2H), 3.78 (s, 3H), 1.98 (d, *J* = 2.2 Hz, 1H), 1.58 (ddd, *J* = 8.9, 5.6, 2.2 Hz, 1H), 1.52 (s, 3H), 1.33 (dd, *J* = 9.0, 4.5, 1H), 0.90 (dd, *J* = 5.5, 4.6, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 137.7, 128.5, 113.8, 84.8, 67.0, 55.3, 26.8, 22.9, 22.6, 14.7 ppm; HRMS (ESI): m/z: calcd for $C_{13}H_{15}O^+$: 187.11174, found: 187.11186.

Experimental procedure for tetrahydrocarbazols ***3*** *and* ***3'***

[{(2-Biphenyl)di-*t*Bu-phosphine}Au(CH_3CN)]SbF_6 (0.0058 mmol, 0.05 eq.) was added to a solution of the corresponding indol (0.232 mmol, 2.0 eq.) and the cyclopropyl alkyne (0.116 mmol, 1.0 eq.) in

toluene (0.1M). The mixture was stirred at 80 °C for 12 h. Then, Et_3N (0.05 eq.) was added to the reaction. The mixture was evaporated in vacuum and the residue was purified by flash chromatography (Hexane:EtOAc) affording the corresponding tetrahydrocarbazol in 42-92% yield.

*Experimental procedure for tetrahydrocarbazols **3** and **3'** with base*

[{(2-Biphenyl)di-*t*Bu-phosphine}Au(CH_3CN)]SbF_6 (0.0058 mmol, 0.05 eq.) was added to a solution of the corresponding indol (0.232 mmol, 2.0 eq.), the cyclopropyl alkyne (0.116 mmol, 1.0 eq.) and $NaHCO_3$ (0.5-1.0 eq.) in toluene (0.1M). The mixture was stirred at 80 °C for 12 h. Then, Et_3N (0.05 eq.) was added to the reaction. The mixture was evaporated in vacuum and the residue was purified by flash chromatography (Hexane:EtOAc) affording the corresponding tetrahydrocarbazol in 34-83% yield.

*9-Benzyl-4-(1-benzyl-1H-indol-3-yl)-1-(4-methoxyphenyl)-4-methyl-2,3,4,9-tetrahydro-1H-carbazole (**3a**)*

Obtained as 2:1 diastereomeric mixture. Characterization of a 1:0.70 diastereomeric ratio. IR (neat, ν/cm^{-1}): 3028, 2929, 2852, 1605, 1507, 1455, 1356, 1321, 1240, 1176, 1037, 835, 736, 695, 562; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 8.1 Hz, 1H, minor isomer), 7.65 (d, *J* = 8.0 Hz, 1H, major isomer), 7.53-7.48 (m, 1H, major and minor isomer), 7.28-6.80 (m, 20H major isomer and 19H minor isomer), 6.68 (d, *J* = 8.7 Hz, 2H, minor isomer), 6.59 (s, 1H, major isomer), 5.31-5.12 (m, 3H, major and minor isomer), 4.76 (d, *J* = 17.0 Hz, 1H, major and minor isomer), 4.02-3.97 (m, 1H, major and minor isomer), 3.80 (s, 3H major isomer), 3.75 (s, 3H, minor isomer), 2.46-2.42 (m, 1H, minor isomer), 2.40-2.34 (m, 1H, major isomer), 2.30-2.20 (m, 1H, minor isomer), 2.14 (s, 3H, major isomer), 2.12-2.07 (m, 1H, major isomer), 2.06 (s, 3H, minor isomer), 2.03-1.99 (m, 1H, minor isomer), 1.96-1.89 (m, 1H, major isomer), 1.83-1.76 (m, 1H, minor isomer), 1.74-1.68 (m, 1H, major isomer) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) (major and minor isomer): δ = 158.2, 158.1, 138.4, 138.3, 138.1, 137.9, 137.6, 137.5, 137.5, 136.5, 136.4, 136.2, 136.1, 129.1, 128.8, 128.6, 128.6, 128.6, 128.5, 127.8, 127.5, 127.3, 127.2, 127.0, 126.9, 126.5, 126.4, 126.3, 126.0, 125.9, 124.1, 123.3, 121.4, 121.3, 121.2, 121.1, 121.0, 120.9, 120.8, 119.5, 119.3, 118.7, 118.6, 118.4, 113.8, 109.9, 109.8, 109.3, 109.2, 55.2, 55.2, 49.7, 49.6, 46.5, 46.3, 38.9, 38.1, 36.7, 36.4, 34.6, 31.3, 30.4, 29.0, 28.1 ppm; MS (ESI): m/z (M^+): 609.4.

*1-(4-Methoxyphenyl)-4,9-dimethyl-4-(1-methyl-1H-indol-3-yl)-2,3,4,9-tetrahydro-1H-carbazole (**3b**)*

Obtained as 2:1 diastereomeric mixture. Characterization of a 1:0.50 diastereomeric ratio. IR (neat, ν/cm^{-1}): 3048, 2921, 2840, 1611, 1509, 1467, 1370, 1244, 1176, 1089, 1031, 907, 835, 731, 562; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 8.0 Hz, 1H, major isomer), 7.70 (d, *J* = 7.9 Hz, 1H, minor isomer), 7.54 (d, *J* = 7.9 Hz, 1H, major isomer), 7.42 (d, *J* = 7.9 Hz, 1H, minor isomer), 7.31 (d, *J* = 8.2 Hz, 1H, major isomer), 7.27 (d, *J* = 8.5 Hz, 1H, major isomer), 7.19 (t, *J* = 7.6 Hz, 2H, major isomer), 7.17-7.13 (m, 2H, minor isomer), 7.08-7.05 (m, 1H major isomer and 2H minor isomer), 7.02-6.98 (m, 2H major isomer and 3H minor isomer), 6.94 (t, *J* = 7.5 Hz, 1H, minor isomer), 6.83 (d, *J* = 8.6 Hz, 2H, major isomer), 6.79 (d, *J* = 8.7 Hz, 2H, minor isomer), 6.72 (s, 1H, minor isomer), 6.33 (s, 1H, major isomer), 4.22-4.18 (m, 1H, major and minor isomer), 3.79 (s, 3H, major isomer), 3.76 (s, 3H, minor

isomer), 3.67 (s, 3H, minor isomer), 3.58 (s, 3H, major isomer), 3.99 (s, 3H, major isomer), 3.35 (s, 3H, minor isomer), 2.43-2.26 (m, 2H, major isomer), 2.14-2.05 (m, 2H, minor isomer), 2.10 (s, 3H, major isomer), 1.99 (s, 3H, minor isomer), 1.97-1.79 (m, 1H major isomer and 2H minor isomer), 1.73-1.69 (m, 1H, major isomer) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2) (major and minor isomer): δ = 158.1, 158.0, 138.0, 137.9, 137.4, 136.8, 136.6, 136.2, 136.1, 129.1, 128.9, 128.8, 127.8, 126.3, 126.1, 125.8, 123.3, 122.3, 121.3, 121.2, 121.1, 121.0, 120.8, 120.7, 120.5, 120.4, 118.8, 118.6, 118.4, 118.3, 118.1, 118.0, 113.9, 113.7, 109.3, 109.2, 108.6, 108.5, 55.2, 39.0, 37.8, 36.8, 36.5, 36.5, 33.9, 32.6, 32.5, 31.2, 29.9, 29.8, 29.4, 29.3, 28.1 ppm; HRMS (ESI): m/z: calcd for $C_{30}H_{30}N_2NaO^+$: 457.2250, found: 457.2247.

*4-(4-Methoxyphenyl)-1,9-dimethyl-1-(1-methyl-1H-indol-3-yl)-2,3,4,9-tetrahydro-1H-carbazole (**3'b**),*

minor diastereoisomer

Obtained as 2:1 diastereomeric mixture. IR (neat, v/cm^{-1}): 3043, 2931, 2846, 2249, 1610, 1508, 1468, 1364, 1324, 1240, 1173, 1035, 1015, 906, 829, 727, 647, 567; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28-7.26 (m, 1H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.15-7.12 (m, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.88-6.84 (m, 7H), 4.32 (dd, *J* = 8.2, 5.6 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.30 (bs, 3H), 2.43-2.37 (m, 1H), 2.19-2.12 (m, 1H), 1.98 (s, 3H), 1.93-1.88 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.9, 142.1, 138.7, 137.7, 137.5, 129.2, 126.4, 126.3, 126.0, 125.8, 121.4, 120.5, 120.5, 119.9, 119.0, 118.4, 113.6, 111.6, 109.1, 108.5, 55.2, 40.6, 40.4, 35.8, 32.7, 32.3, 30.7, 26.9 ppm; MS (ESI): m/z [M+Na]$^+$: 457.2.

*4-(4-Methoxyphenyl)-1,9-dimethyl-1-(1-methyl-1H-indol-3-yl)-2,3,4,9-tetrahydro-1H-carbazole (**3'b**),*

major diastereoisomer

Obtained as 2:1 diastereomeric mixture. IR (neat, v/cm^{-1}): 3043, 2931, 2846, 2249, 1610, 1508, 1468, 1364, 1324, 1240, 1173, 1035, 1015, 906, 829, 727, 647, 567; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35-6.85 (m, 13H), 4.38-4.34 (m, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 3.51 (bs, 3H), 2.51-2.46 (m, 1H), 2.39-2.28 (m, 1H), 2.04 (s, 3H), 1.99-1.90 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.7, 142.2, 138.3, 137.6, 137.5, 129.2, 126.7, 126.6, 125.9, 122.0, 121.3, 120.8, 120.7, 119.7, 118.7, 118.7, 113.5, 111.6, 109.2, 108.6, 55.1, 39.9, 36.2, 32.6, 31.3, 30.9, 30.7, 27.2 ppm; MS (ESI): m/z [M+Na]$^+$: 457.2.

*4-(1H-Indol-3-yl)-1-(4-methoxyphenyl)-4-methyl-2,3,4,9-tetrahydro-1H-carbazole (**3c**)*

Obtained as 1:1 diastereomeric mixture. Characterization of a 1: 0.81 diastereomeric ratio. IR (neat, v/cm^{-1}): 3408, 3054, 2933, 2846, 1611, 1509, 1455, 1304, 1240, 1175, 1101, 1031, 1013, 906, 830, 728; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.0 Hz, 1H, major isomer), 7.85 (s, 1H, minor isomer), 7.78 (s, 1H, major isomer), 7.52 (d, *J* = 8.0 Hz, 1H, major isomer), 7.49 (d, *J* = 8.6 Hz, 2H, minor isomer), 7.40-6.81 (m, 9H major isomer and 12H minor isomer), 6.60 (d, *J* = 2.3 Hz, 1H, major isomer), 4.25-4.22 (m, 1H, minor isomer), 4.10 (dd, *J* = 10.5, 5.7 Hz, 1H, major isomer), 3.84 (s, 3H, minor isomer), 3.80 (s, 3H, major isomer), 2.73-2.69 (m, 1H, major isomer), 2.53-2.48 (m, 1H, minor isomer), 2.22-2.15 (m, 1H, major isomer), 2.12 (s, 3H, major isomer), 2.04 (s, 3H, minor isomer), 2.02-1.97 (m, 1H major isomer and 3H minor isomer), 1.80-1.71 (m, 1H, major isomer) ppm; ^{13}C NMR

(100 MHz, $CDCl_3$): δ = 158.5 (2x), 137.4, 137.2, 136.6, 136.2, 136.1, 136.0, 135.9, 135.4, 129.3, 129.2, 127.3, 126.9, 126.8, 125.930, 125.4, 125.0, 124.3, 124.2, 121.9, 121.3, 121.3, 121.0, 120.9, 120.9, 120.8, 120.3, 118.9, 118.8, 118.7, 118.7, 118.5, 114.1, 114.0, 111.4, 111.1, 110.6, 110.5, 55.3, 55.2, 41.7, 40.7, 38.6, 37.6, 36.8, 35.6, 30.9, 30.7, 28.8, 27.7 (one carbon missing due to overlapping) ppm; HRMS (ESI): m/z: calcd for $C_{28}H_{26}N_2NaO^+$: 429.1937, found: 429.1935.

*1-(1H-Indol-3-yl)-4-(4-methoxyphenyl)-1-methyl-2,3,4,9-tetrahydro-1H-carbazole (**3'c**), isomer 1*

IR (neat, v/cm^{-1}): 3400, 3051, 2926, 2854, 1614, 1508, 1457, 1332, 1306, 1240, 1175, 1103, 1031, 1012, 831, 735; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.84 (s, 1H), 7.78 (s, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 1H), 7.18-7.16 (m, 1H), 7.13 (d, *J* = 8.5 Hz, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.01 (t, *J* = 7.3 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.88-6.82 (m, 2H), 6.75-7.72 (m, 3H), 4.15 (t, *J* = 6.7 Hz, 1H), 3.70 (s, 3H), 2.52-2.47 (m, 1H), 2.16-2.11 (m, 1H), 1.88-1.83 (m, 1H), 1.85 (s, 3H), 1.78-1.72 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.8, 141.4, 138.3, 137.1, 135.9, 129.1, 127.3, 125.2, 123.6, 122.8, 121.8, 121.2, 120.7, 119.9, 119.3, 119.0, 113.6, 112.0, 111.4, 110.6, 55.2, 39.3, 36.9, 36.2, 31.4, 27.7 ppm; HRMS (ESI): m/z: calcd for $C_{28}H_{26}N_2NaO^+$: 429.1937, found: 429.1936.

*1-(1H-Indol-3-yl)-4-(4-methoxyphenyl)-1-methyl-2,3,4,9-tetrahydro-1H-carbazole (**3'c**), isomer 2*

IR (neat, v/cm^{-1}): 3405, 3051, 2926, 2854, 1614, 1508, 1455, 1327, 1265, 1240, 1175, 1103, 1030, 1011, 835, 739; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (s, 1H), 7.64 (s, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.23 (d, *J* = 8.6 Hz, 2H), 7.16-7.08 (m, 3H), 7.04-7.01 (m, 2H), 6.92-6.84 (m, 5H), 4.33 (dd, *J* = 8.3, 5.7 Hz, 1H), 3.83 (s, 3H), 2.57-2.50 (m, 1H), 2.27-2.19 (m, 1H), 2.06-1.90 (m, 2H), 1.95 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.9, 141.9, 138.5, 136.9, 135.9, 129.0, 127.2, 125.5, 123.4, 121.9, 121.8, 120.9, 120.5, 119.9, 119.6, 118.8, 113.7, 111.7, 111.2, 110.6, 55.2, 39.9, 37.6, 35.6, 32.3, 27.6 ppm; HRMS (ESI): m/z: calcd for $C_{28}H_{26}N_2NaO^+$: 429.1937, found: 429.1936.

*9-(4-Methoxybenzyl)-4-(1-(4-methoxybenzyl)-1H-indol-3-yl)-1-(4-methoxyphenyl)-4-methyl-2,3,4,9-tetrahydro-1H-carbazole (**3d**)*

Obtained as 2:1 diastereomeric mixture. Characterization of a 1:0.63 diastereomeric ratio. IR (neat, v/cm^{-1}): 3048, 3002, 2931, 2834, 1610, 1509, 1462, 1353, 1326, 1243, 1173, 1033, 828, 731, 535; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 8.2 Hz, 1H, minor isomer), 7.59 (d, *J* = 7.9 Hz, 1H, major isomer), 7.47-7.43 (m, 1H major and minor isomer), 7.22-6.52 (m, 16H major isomer and 13H minor isomer), 6.52 (s, 1H, major isomer), 5.19-5.01 (m, 6H, major and minor isomer), 4.68-4.63 (m, 2H, major and minor isomer), 3.99-3.94 (m, 1H, major and minor isomer), 3.76 (s, 3H, major isomer), 3.72 (s, 3H, minor isomer), 3.71 (s, 3H, major isomer), 3.71 (s, 3H, major isomer), 3.70 (s, 3H, minor isomer), 3.70 (s, 3H, minor isomer), 2.41-2.29 (m, 1H, major and minor isomer), 2.23-2.14 (m, 1H, major isomer), 2.09 (s, 3H, major isomer), 2.06-2.4 (m, 1H, minor isomer), 2.00 (s, 3H, minor isomer), 1.97-1.94 (m, 1H, minor isomer), 1.92-1.88 (m, 1H, major isomer), 1.77-1.64 (m, 2H, major isomer) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2) (major and minor isomer): δ = 158.9, 158.8, 158.7, 158.6, 158.2, 158.1, 157.9, 137.5, 137.5, 137.5, 137.4, 136.5, 136.5, 136.2, 136.1, 130.5, 130.3, 130.1, 129.9, 129.1, 128.8, 127.8, 127.7, 127.4, 127.2, 127.1, 126.8, 126.5, 126.4, 126.4, 126.3, 124.0, 123.2,

121.4, 121.3, 121.2, 121.1, 121.0, 120.9, 120.8, 120.7, 119.5, 119.3, 118.6, 118.5, 118.4, 114.1, 114.1, 114.0, 113.9, 113.9, 113.8, 109.9, 109.8, 109.3, 109.2, 55.2, 55.2, 55.1, 49.2, 49.1, 45.9, 45.8, 38.9, 38.1, 36.7, 36.4, 34.6, 31.3, 30.4, 29.7, 29.1, 28.1 ppm; HRMS (ESI): m/z: calcd for $C_{44}H_{42}N_2NaO_3^+$: 669.3087, found: 669.3087.

*9-Cinnamyl-4-(1-cinnamyl-1H-indol-3-yl)-1-(4-methoxyphenyl)-4-methyl-2,3,4,9-tetrahydro-1H-carbazole (**3e**)*

Obtained as 2:1 diastereomeric mixture. Characterization of a 1:0.57 diastereomeric ratio. IR (neat, v/cm^{-1}): 3056, 3020, 2952, 2932, 2854, 1609, 1509, 1463, 1355, 1327, 1246, 1176, 1032, 965, 908, 833, 733, 692; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 8.0 Hz, 1H, minor isomer), 7.74 (d, *J* = 8.0 Hz, 1H, major isomer), 7.55 (d, *J* = 7.9 Hz, 1H, major isomer), 7.50 (d, *J*= 7.9 Hz, 1H, minor isomer), 7.36-6.92 (m, 22H major isomer and 18H minor isomer), 6.84-6.82 (m, 2H major isomer and 1H minor isomer), 6.65 (d, *J* = 8.6 Hz, 2H, minor isomer), 6.51 (s, 1H, major isomer), 6.35-5.87 (m, 4H, major and minor isomer), 4.86-4.63 (m, 3H, major and minor isomer), 4.50-4.39 (m, 1H, major and minor isomer), 4.24 (dd, *J* = 5.4, 2.5 Hz, 1H, major isomer), 4.21 (t, *J* = 6.1 Hz, 1H, minor isomer), 3.74 (s, 3H, major isomer), 3.56 (s, 3H, minor isomer), 2.50-2.38 (m, 1H, major and minor isomer), 2.34-2.27 (m, 1H, minor isomer), 2.20-2.12 (m, 1H, major isomer), 2.15 (s, 3H, major isomer), 2.06 (s, 3H, minor isomer), 2.02-1.94 (m, 1H, major and minor isomer), 1.87-1.80 (m, 1H, minor isomer), 1.77-1.72 (m, 1H, major isomer) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) (major and minor isomer): 158.2, 158.1, 137.5, 137.4, 137.1, 137.0, 136.7, 136.5, 136.5, 136.4, 136.4, 136.4, 136.2, 136.0, 131.5, 131.3, 131.1, 131.0, 129.4, 129.0, 128.5, 128.5, 128.4, 128.4, 127.9, 127.6, 127.6, 127.5, 127.5, 127.2, 127.2, 126.6, 126.4, 126.4, 126.4, 126.3, 126.3, 126.3, 125.5, 125.4, 125.3, 125.3, 123.9, 122.9, 121.4, 121.3, 121.2, 121.2, 121.0, 120.9, 120.7, 120.7, 119.2, 118.9, 118.6, 118.5, 118.4, 118.3, 113.9, 113.8, 109.8, 109.6, 109.3, 109.2, 55.1, 55.0, 48.0, 47.8, 45.5, 45.0, 39.1, 37.9, 36.7, 36.5, 34.2, 30.1, 29.4, 28.1, 22.3, 14.0 ppm; HRMS (ESI): m/z: calcd for $C_{46}H_{42}N_2NaO^+$: 661.3189, found: 661.3187.

*1-(4-Methoxyphenyl)-4-methyl-9-pentyl-4-(1-pentyl-1H-indol-3-yl)-2,3,4,9-tetrahydro-1H-carbazole (**3f**)*

Obtained as 2:1 diastereomeric mixture. Characterization of a 1:1 diastereomeric ratio. IR (neat, v/cm^{-1}): 3046, 2955, 2929, 2870, 1609, 1509, 1464, 1363, 1327, 1244, 1174, 1104, 1035, 906, 831, 728, 648; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.31-7.27 (m, 4H), 7.18-7.11 (m, 4H), 7.07-7.00 (m, 6H), 6.98-6.92 (m, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.78-6.74 (m, 3H), 6.37 (s, 1H), 4.20-4.16 (m, 2H), 4.00 (t, *J* = 7.2 Hz, 2H), 3.94-3.89 (m, 2H), 3.88-3.82 (m, 2H), 3.80 (s, 3H), 3.75 (s, 3H), 3.73-3.60 (m, 2H), 2.42-2.24 (m, 3H), 2.11 (s, 3H), 2.09-2.02 (m, 1H), 2.00 (s, 3H), 1.92 (dt, *J* = 13.0, 2.1 Hz, 1H), 1.80-1.63 (m, 7H), 1.42-1.06 (m, 20H), 0.87-0.81 (m, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.2, 158.1, 137.2, 137.1, 136.9, 136.8, 136.7, 136.4, 136.3, 135.9, 130.9, 129.2, 128.9, 127.9, 127.2, 126.5, 126.4, 126.2, 126.1, 123.2, 122.6, 122.2, 121.4, 121.3, 121.1, 120.6, 120.5, 120.3, 118.6, 118.4, 118.2, 118.1, 117.9, 117.9, 113.8, 113.7, 109.5, 109.4, 109.1, 109.0, 55.2, 55.2, 47.7, 46.1, 45.9, 43.6, 43.2, 39.2, 38.1, 36.6, 36.5, 34.0, 31.3, 31.3, 30.0, 29.9, 29.9, 29.7, 29.5, 29.4, 29.4, 29.2, 29.1, 29.1, 29.0, 28.1, 22.4, 22.3, 22.291, 22.2, 13.9, 13.9 ppm; HRMS (ESI): m/z: calcd for $C_{38}H_{46}N_2NaO^+$: 569.3502, found: 569.3496.

*6-Methoxy-4-(5-methoxy-1-methyl-1H-indol-3-yl)-1-(4-methoxyphenyl)-4,9-dimethyl-2,3,4,9-tetrahydro-1H-carbazole (**3g**)*

IR (neat, v/cm^{-1}): 2932, 2832, 1614, 1577, 1509, 1484, 1452, 1245, 1213, 1176, 1150, 1040, 910, 837, 790, 727; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20-7.15 (m, 3H), 7.01-6.97 (m, 3H), 6.88-6.82 (m, 4H), 6.35 (s, 3H), 4.18-4.17 (m, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 3.74 (s, 3H), 3.57 (s, 3H), 3.36 (s, 3H), 2.36-2.29 (m, 1H), 2.13-2.05 (m, 1H), 2.07 (s, 3H), 1.86 (dt, *J* = 13.0, 1.65 Hz, 1H), 1.73-1.69 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.1, 153.2, 152.9, 136.9, 136.1, 133.6, 132.9, 129.6, 129.1, 126.6, 126.1, 121.4, 118.2, 113.7, 110.4, 110.2, 109.8, 109.1, 103.9, 103.9, 56.1, 56.1, 55.2, 37.9, 36.4, 33.8, 32.6, 29.9, 29.4, 29.1 ppm; HRMS (ESI): m/z: calcd for $C_{32}H_{34}rN_2NaO_3^+$: 517.2462, found: 517.2461.

*9-Benzyl-4-(1-benzyl-5-methoxy-1H-indol-3-yl)-6-methoxy-1-(4-methoxyphenyl)-4-methyl-2,3,4,9-tetrahydro-1H-carbazole (**3h**)*

Obtained as 2:1 diastereomeric mixture. Characterization of a 1:0.40 diastereomeric ratio. IR (neat, v/cm^{-1}): 3054, 3031, 2931, 2829, 1616, 1575, 1509, 1482, 1451, 1353, 1299, 1245, 1215, 1175, 1035, 909, 834, 793, 732, 702; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25-6.18 (m, 20H, major and minor isomer), 6.68 (d, *J* = 8.7 Hz, 2H, minor isomer), 6.57 (s, 1H, major isomer), 5.23 (d, *J* = 6.6 Hz, 1H, minor isomer), 5.16 (s, 2H, major isomer), 5.07 (d, *J* = 17.0 Hz, 1H, major and minor isomer), 4.77 (d, *J* = 17.0 Hz, 1H, major isomer), 4.74 (d, *J* = 17.1 Hz, 1H, minor isomer), 4.02 (dd, *J* = 5.4, 2.9 Hz, 1H, major isomer), 3.98 (t, *J* = 5.7 Hz, 1H, minor isomer), 3.80 (s, 3H, major isomer), 3.78 (s, 3H, major isomer), 3.77 (s, 3H, minor isomer), 3.74 (s, 3H, minor isomer), 3.68 (s, 3H, major isomer), 3.62 (s, 3H, minor isomer), 2.43-2.35 (m, 1H, major and minor isomer), 2.30-2.22 (m, 1H, minor isomer), 2.12 (s, 3H, major isomer), 2.10-2.04 (m, 1H, major isomer), 2.03 (s, 3H, minor isomer), 2.01-1.96 (m, 1H, minor isomer), 1.91 (dt, *J* =12.9, 1.9 Hz, 1H, major isomer), 1.82-1.77 (m, 1H, minor isomer), 1.73-1.68 (m, 1H, major isomer) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) (major and minor isomer): 158.2, 158.1, 153.3, 153.2, 153.1, 138.4, 138.4, 138.2, 138.0, 137.2, 136.9, 136.6, 136.1, 133.0, 132.9, 132.7, 132.6, 129.1, 128.9, 128.8, 128.6, 128.6, 128.5, 128.4, 128.1, 127.3, 127.3, 127.0, 126.9, 126.8, 126.7, 126.6, 126.6, 126.4, 126.3, 125.9, 123.3, 122.3, 119.1, 118.8, 113.8, 113.8, 111.0, 110.7, 110.6, 110.5, 110.4, 110.4, 109.9, 109.8, 104.2, 104.0, 103.5, 103.5, 56.0, 56.0, 55.8, 55.7, 55.2, 55.2, 49.9, 49.8, 46.6, 46.5, 39.0, 38.1, 36.4, 36.3, 34.1, 31.2, 30.2, 29.7, 28.9, 27.7 ppm (two carbon are missing due to overlapping); HRMS (ESI): m/z: calcd for $C_{44}H_{42}N_2NaO_3^+$: 669.3087, found: 669.3086.

*6-Bromo-4-(5-bromo-1-methyl-1H-indol-3-yl)-1-(4-methoxyphenyl)-4,9-dimethyl-2,3,4,9-tetrahydro-1H-carbazole (**3i**)*

Obtained as 2:1 diastereomeric mixture. IR (neat, v/cm^{-1}): 2931, 2855, 1609, 1509, 1469, 1420, 1370, 1245, 1176, 1096, 1035, 986, 907, 788, 730; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.72 (s, 1H, major isomer), 7.63 (s, 1H, minor isomer), 7.56 (s, 1H, major isomer), 7.30 (s, 1H, minor isomer), 7.25-7.15 (m, 4H, major and minor isomer), 7.09 (d, *J* = 8.3 Hz, 2H, minor isomer), 6.97 (d, *J* = 8.4 Hz, 2H, major isomer), 6.91 (s, 1H, major isomer), 6.89 (s, 1H, minor isomer), 6.84 (d, *J* = 8.4 Hz, 2H, major isomer) 6.39 (s, 1H, major isomer), 4.26-4.21 (m, 1H, major and minor isomer), 3.78 (s, 3H, major isomer), 3.77 (s, 3H, minor isomer), 3.59 (s, 3H, major isomer), 3.37 (s, 3H, minor isomer), 3.35 (s, 3H, major isomer), 2.46-2.39 (m, 1H, minor isomer), 2.31-2.19 (m, 1H, major and minor isomer), 2.11-2.06 (m, 1H, major and minor isomer), 2.03 (s, 3H, major isomer), 1.96-1.89 (m, 1H, major and minor isomer), 1.86 (s, 3H, minor isomer), 1.76-1.71 (m, 1H, major and minor isomer) ppm; ^{13}C NMR (100 MHz,

CD_2Cl_2) (major and minor isomer): δ = 158.9, 158.8, 138.5, 138.4, 137.3, 137.2, 136.8, 136.7, 136.4, 136.2, 130.3, 129.6, 129.3, 129.1, 128.4, 128.2, 128.1, 124.2, 124.1, 123.8, 123.8, 123.7, 123.6, 123.5, 123.4, 122.8, 122.4, 118.5, 114.7, 114.4, 112.2, 112.1, 112.1, 111.9, 111.5, 111.4, 110.9, 55.7, 38.6, 38.4, 36.7, 36.5, 36.3, 34.9, 33.3, 33.2, 31.1, 30.4, 30.3, 30.1, 29.5, 27.9 ppm; HRMS (ESI): m/z: calcd for $C_{30}H_{28}Br_2N_2NaO^+$: 613.0457, found: 613.0460.

*9-Benzyl-4-(1-benzyl-5-bromo-1H-indol-3-yl)-6-bromo-1-(4-methoxyphenyl)-4-methyl-2,3,4,9-tetrahydro-1H-carbazole (**3j**)*

Obtained as 2:1 diastereomeric mixture. IR (neat, v/cm^{-1}): 3062, 3028, 2930, 2857, 2835, 1606, 1508, 1463, 1452, 1353, 1245, 1176, 1031, 988, 907, 831, 790, 696; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.8 (s, 1H, minor isomer), 7.68 (s, 1H, major isomer), 7.55 (s, 1H, major isomer), 7.48 (s, 1H, minor isomer), 7.35-7.32 (m, 2H, major and minor isomer), 7.27-6.97 (m, 12H major isomer and 13H minor isomer), 6.85-6.77 (m, 4H, major and minor), 6.66 (s, 1H, major isomer), 5.33-5.19 (m, 2H major and minor isomer), 5.12 (d, *J* = 17.1 Hz, 1H, minor isomer), 5.07 (d, *J* = 17.1 Hz, 1H, major isomer), 4.82 (d, *J* = 17.1 Hz, 1H, minor isomer), 4.73 (d, *J* = 17.1 Hz, 1H, major isomer), 4.04-4.02 (m, 1H major and minor isomer), 3.82 (s, 3H, major isomer), 3.77 (s, 3H, minor isomer), 2.37-2.29 (m, 2H, major isomer), 2.12-2.09 (m, 2H, minor isomer), 2.06 (s, 3H, major isomer), 1.95 (s, 3H, minor isomer), 1.92-1.81 (m, 1H major isomer and 2H minor isomer), 1.78-1.76 (m, 1H, major isomer) ppm; ^{13}C NMR (125 MHz, CD_2Cl_2) (major and minor isomer): δ = 158.2, 158.1, 137.7, 137.6, 137.5, 137.4, 137.2, 136.1, 136.0, 136.0, 135.6, 135.5, 128.9, 128.9, 128.8, 128.7, 128.6, 128.5, 127.9, 127.8, 127.8, 127.5, 127.4, 127.2, 127.1, 126.2, 126.1, 125.8, 125.7, 124.1, 124.0, 123.8, 123.7, 123.5, 123.3, 122.9, 122.8, 122.6, 118.6, 118.5, 114.1, 113.9, 112.1, 112.0, 111.9, 111.4, 111.3, 110.9, 110.8, 55.2, 55.2, 49.9, 49.9, 46.6, 46.5, 38.2, 38.0, 35.9, 35.8, 35.6, 34.9, 30.5, 28.8, 27.6 ppm; HRMS (ESI): m/z: calcd for $C_{42}H_{36}Br_2N_2NaO^+$: 765.1087, found: 765.1088.

*4-(1,5-Dimethyl-1H-indol-3-yl)-1-(4-methoxyphenyl)-4,6,9-trimethyl-2,3,4,9-tetrahydro-1H-carbazole (**3k**)*

Obtained as 2:1 diastereomeric mixture. Characterization of a 1:0.63 diastereomeric ratio. IR (neat, v/cm^{-1}): 3032, 2929, 2866, 1609, 1508, 1486, 1461, 1371, 1245, 1175, 1092, 1034, 908, 833, 790, 731; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (s, 1H, major isomer), 7.55 (s, 1H, minor isomer), 7.38 (s, 1H, major isomer), 7.06-6.96 (m, 4H major isomer and 5H minor isomer), 7.22-7.14 (m, 3H major isomer and 2H minor isomer), 6.83-6.78 (m, 2H major and minor isomer), 6.67 (s, 1H, minor isomer), 6.25 (s, 1H, major isomer), 4.18-4.15 (m, 1H, major and minor isomer), 3.79 (s, 3H, major isomer), 3.77 (s, 3H, minor isomer), 3.65 (s, 3H, minor isomer), 3.55 (s, 3H, major isomer), 3.37 (s, 3H, major isomer), 3.30 (s, 3H, minor isomer), 2.48 (s, 3H, major isomer), 2.44 (s, 3H, minor isomer), 2.39 (s, 3H, major isomer), 2.35 (s, 3H, minor isomer), 2.31-2.21 (m, 1H, major and minor isomer), 2.11 (s, 3H, major isomer), 2.09-2.03 (m, 1H, major isomer), 1.99 (s, 3H, minor isomer), 1.96-1.92 (m, 1H, minor isomer), 1.89-1.77 (m, 1H, major and minor isomer), 1.70-1.66 (m, 1H, major isomer) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2) (major and minor isomer): δ = 158.1, 158.0, 137.0, 136.8, 136.5, 136.4, 136.3, 136.2, 135.9, 135.8, 129.4, 129.2, 128.8, 128.2, 127.4, 127.3, 127.2, 127.1, 126.5, 126.4, 125.9, 122.7, 122.4, 122.3, 122.0, 121.9, 121.6, 121.2, 121.0, 121.0, 120.8, 118.4, 118.2, 113.9, 113.7, 110.0, 109.1, 108.9, 108.3, 108.2, 55.3, 55.2, 39.3, 39.3, 37.7, 36.9, 36.6, 36.6, 33.5, 32.6, 32.5, 31.4, 30.1, 29.7, 29.5, 29.3, 28.2, 21.7, 21.6, 21.5 ppm; HRMS (ESI): m/z: calcd for $C_{22}H_{34}N_2NaO^+$: 485.2563, found: 485.2560.

*9-Benzyl-4-(1-benzyl-5-methyl-1H-indol-3-yl)-1-(4-methoxyphenyl)-4,6-dimethyl-2,3,4,9-tetrahydro-1H-carbazole (**3l**), major diastereoisomer*

Obtained as 2:1 diastereomeric mixture. IR (neat, ν/cm^{-1}): 3056, 3025, 2928, 2858, 1608, 1508, 1495, 1481, 1453, 1372, 1354, 1300, 1246, 1177, 1033, 909, 834, 789, 732, 701; ^{1}H NMR (500 MHz, $CDCl_3$)(major diastereoisomer): δ = 7.52 (s, 1H), 7.34 (s, 1H), 7.23 (d, *J* = 7.5 Hz, 2H), 7.20 (d, *J* = 7.1 Hz, 1H), 7.17-7.16 (m, 3H), 7.09 (t, *J* = 7.8 Hz, 2H), 7.0-6.97 (m, 3H), 6.95-6.90 (m, 2H), 6.86-6.84 (m, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 6.52 (s, 1H), 5.20-5.13 (m, 2H), 5.08 (d, *J* = 17.0 Hz, 1H), 4.74 (d, *J* = 17.0 Hz, 1H), 4.00 (dd, *J* = 5.4, 2.8 Hz, 1H), 3.80 (s, 3H), 2.43 (s, 3H), 2.41-2.34 (m, 1H), 2.34 (s, 3H), 2.13 (s, 3H), 2.10-2.04 (m, 1H), 1.90 (dt, *J* = 13.0, 2.1 Hz, 1H), 1.69-1.65 (m, 1H) ppm; ^{13}C NMR (125 MHz, CD_2Cl_2): 158.2, 138.6, 138.1, 136.2, 136.2, 136.0, 135.8, 129.2, 128.6, 128.6, 128.4, 127.7, 127.5, 127.2, 126.9, 126.7, 126.5, 126.3, 125.9, 122.6, 122.5, 122.3, 121.1, 120.9, 118.8, 113.8, 109.6, 109.0, 55.2, 49.7, 46.3, 37.9, 36.4, 34.2, 30.2, 29.2, 21.7, 21.5 ppm; HRMS (ESI): m/z: calcd for $C_{44}H_{42}N_2NaO^+$: 637.3189, found: 637.3192.

*9-Benzyl-4-(1-benzyl-5-methyl-1H-indol-3-yl)-1-(4-methoxyphenyl)-4,6-dimethyl-2,3,4,9-tetrahydro-1H-carbazole (**3l**), minor diastereoisomer*

Obtained as 2:1 diastereomeric mixture. IR (neat, ν/cm^{-1}): 3056, 3025, 2928, 2858, 1608, 1508, 1495, 1481, 1453, 1372, 1354, 1300, 1246, 1177, 1033, 909, 834, 789, 732, 701; ^{1}H NMR (500 MHz, $CDCl_3$)(major diastereoisomer): δ = 7.59 (s, 1H), 7.30 (s, 1H), 7.24-6.80 (m, 17H), 6.68 (d, *J* = 8.3 Hz, 2H), 5.23 (dd, *J* = 30.4, 16.5 Hz, 2H), 5.09 (d, *J* = 17.0 Hz, 1H), 4.74 (d, *J* = 17.1 Hz, 1H), 3.97 (t, *J* = 5.8 Hz, 1H), 3.74 (s, 3H), 2.45-2.40 (m, 1H), 2.42 (s, 3H), 2.32 (s, 3H), 2.28-2.19 (m, 1H), 2.03 (s, 3H), 2.00-1.95 (m, 1H), 1.82-1.77 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): 158.0, 138.5, 138.3, 136.6, 136.5, 135.9, 135.9, 128.9, 128.6, 128.5, 127.7, 127.6, 127.4, 127.1, 126.8, 126.6, 126.5, 126.2, 125.9, 123.4, 122.7, 122.2, 121.1, 121.1, 119.1, 113.8, 109.5, 108.9, 55.2, 49.6, 46.5, 38.8, 36.6, 36.4, 31.2, 28.0, 21.5, 21.5 ppm (one carbon is missing due to overlapping); HRMS (ESI): m/z: calcd for $C_{44}H_{42}N_2NaO^+$: 637.3189, found: 637.3192.

*5-(5-Cyano-1-methyl-1H-indol-3-yl)-8-(4-methoxyphenyl)-5,9-dimethyl-6,7,8,9-tetrahydro-5H-carbazole-3-carbonitrile (**3m**), major diastereoisomer*

IR (neat, ν/cm^{-1}): 2963, 2926, 2858, 2217, 1609, 1509, 1482, 1375, 1245, 1176, 1091, 1033, 907, 801, 718; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (s, 1H), 7.62 (s, 1H), 7.40-7.36 (m, 2H), 7.33-7.30 (m, 2H), 6.99 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 6.63 (s, 1H), 4.26 (t, *J* = 4.8 Hz, 1H), 3.81 (s, 3H), 3.72 (s, 3H), 3.40 (s, 3H), 2.27-2.22 (m, 1H), 2.18-2.10 (m, 1H), 2.02 (s, 3H), 1.96-1.83 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.4, 139.4, 139.0, 135.2, 129.6, 128.8, 126.3, 125.6, 125.5, 124.1, 123.9, 123.7, 121.1, 121.0, 118.9, 114.2, 110.3, 109.7, 101.5, 101.4, 55.3, 38.3, 35.8, 35.6, 32.9, 30.4, 30.1, 29.1(two carbon missing due to overlapping) ppm; HRMS (ESI): m/z: calcd for $C_{32}H_{28}N_4NaO^+$: 507.2155, found: 507.22151.

*5-(5-Cyano-1-methyl-1H-indol-3-yl)-8-(4-methoxyphenyl)-5,9-dimethyl-6,7,8,9-tetrahydro-5H-carbazole-3-carbonitrile (**3m**),minor diastereoisomer*

IR (neat, v/cm^{-1}): 2963, 2926, 2858, 2217, 1609, 1509, 1482, 1375, 1245, 1176, 1091, 1033, 907, 801, 718; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (s, 1H), 7.39 (s, 1H), 7.35-7.29 (m, 4H), 7.09-7.07 (m, 3H), 6.96 (d, *J* = 8.6 Hz, 2H), 4.29 (dd, *J* = 5.7. 3.1 Hz, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 3.49 (s, 3H), 2.56-2.48 (m, 1H), 2.32-2.23 (m, 1H), 2.11-2.07 (m, 1H), 1.85 (s, 3H), 1.72-1.68 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.5, 139.3, 138.9, 138.6, 134.6, 128.7, 128.6, 126.5, 125.6, 125.1, 124.3, 124.1, 124.0, 121.2, 120.9, 118.8, 114.4, 110.3, 109.7, 101.4, 101.3, 55.3, 37.3, 37.3, 35.5, 33.1, 30.1, 29.9, 27.4 ppm; HRMS (ESI): m/z: calcd for $C_{32}H_{28}N_4NaO^+$: 507.2155, found: 507.22151.

*(E)-9-Benzyl-4-(1-benzyl-1H-indol-3-yl)-4-methyl-1-(1-phenylprop-1-en-2-yl)-2,3,4,9-tetrahydro-1H-carbazole (**3n**)*

Obtained as 1:1 diastereomeric mixture. Characterization of a 1:0.5 diastereomeric ratio. IR (neat, v/cm^{-1}): 3084, 3047, 3027, 2929, 2857, 1604, 1463, 1453, 1354, 1327, 1178, 1074, 1027, 908, 729, 697; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.0 Hz, 1H, major isomer), 7.63 (d, *J* = 7.5 Hz, 1H, minor isomer), 7.47-7.38 (m, 1H, major and minor isomer), 7.33-6.91 (m, 23H, major and minor isomer), 6.84 (s, 1H, major isomer), 6.61 (s, 1H, minor isomer), 6.24 (s, 1H, major isomer), 6.08 (s, 1H, minor isomer), 5.41-5.16 (m, 4H, major and minor isomer), 3.55 (t, *J* = 5.6 Hz, 1H, major isomer), 3.49-3.47 (m, 1H, minor isomer), 2.61-2.55 (m, 1H, major isomer), 2.48-2.42 (m, 1H, minor isomer), 2.09 (s, 3H, minor isomer), 2.06-2.00 (m, 1H, major isomer), 2.02 (s, 3H, major isomer), 1.95 (s, 3H, minor isomer), 1.92-1.86 (m, 1H, minor isomer), 1.77 (s, 3H, major isomer) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.8, 139.5, 138.5, 138.4, 138.1, 138.0, 137.9, 137.9, 137.6, 137.5, 137.4, 135.8, 135.7, 128.9, 128.8, 128.7, 128.6, 128.6, 128.5, 128.3, 128.2, 128.0, 128.0, 127.9, 127.7, 127.4, 127.3, 127.2, 127.1, 127.0, 126.4, 126.2, 126.1, 126.0, 126.0, 125.8, 125.6, 123.9, 121.4, 121.2, 121.1, 121.1, 120.8, 120.8, 119.7, 119.5, 118.6, 118.4, 109.9, 109.8, 109.3, 109.3, 49.7, 46.6, 43.4, 42.6, 36.6, 36.5, 36.3, 35.2, 29.7, 28.9, 28.2, 28.1, 26.1, 25.4, 17.6, 16.6 ppm (eight carbon are missing due to overlapping); HRMS (ESI): m/z: calcd for $C_{44}H_{40}N_2Na^+$: 619.3083, found: 619.3080.

*(E)-5-(5-Cyano-1-methyl-1H-indol-3-yl)-5,9-dimethyl-8-(1-phenylprop-1-en-2-yl)-6,7,8,9-tetrahydro-5H-carbazole-3-carbonitrile (**3o**), major diastereoisomer*

IR (neat, v/cm^{-1}): 2932, 2858, 2216, 1609, 1482, 1446, 1375 1228, 1139, 1087, 909, 802, 730; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (s, 1H), 7.59 (s, 1H), 7.40-7.31 (m, 6H), 7.23-7.22 (m, 3H), 6.63 (s, 1H), 6.01 (s, 1H), 3.75-3.69 (m, 1H), 3.72 (s, 6H), 2.33-2.28 (m, 1H), 2.09-1.94 (m, 3H), 2.01 (s, 3H), 1.99 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.3, 139.0, 138.7, 138.6, 137.6, 129.6, 128.7, 128.3, 128.2, 126.5, 126.3, 125.6, 124.1, 123.9, 123.6, 121.1, 121.0, 119.0, 110.3, 109.6, 101.5, 101.4, 42.5, 35.9, 35.8, 32.9, 29.9, 29.0, 25.2, 17.4 (two carbon missing due to overlapping) ppm; HRMS (ESI): m/z: calcd for $C_{34}H_{30}N_4Na^+$: 517.2363, found: 517.2362.

*(E)-5-(5-Cyano-1-methyl-1H-indol-3-yl)-5,9-dimethyl-8-(1-phenylprop-1-en-2-yl)-6,7,8,9-tetrahydro-5H-carbazole-3-carbonitrile (**3o**), minor diastereoisomer*

IR (neat, ν/cm^{-1}): 2933, 2854, 2217, 1728, 1610, 1483, 1447, 1375, 1289, 1234, 1148, 1095, 910, 802, 730, 699; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (s, 1H), 7.44 (s, 1H), 7.38-7.30 (m, 6H), 7.24-7.18 (m, 3H), 6.90 (s, 1H), 6.19 (s, 1H), 3.78 (s, 3H), 3.71 (s, 3H), 3.71-3.68 (m, 1H), 2.43-2.36 (m, 1H), 2.29-2.20 (m, 1H), 2.02-1.95 (m, 1H), 2.00 (s, 3H), 1.87 (s, 3H), 1.85-1.83 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.2, 138.9, 138.8, 138.4, 137.3, 128.9, 128.8, 128.2, 126.6, 126.1, 125.5, 125.4, 125.3, 124.3, 124.1, 124.0, 121.2, 120.8, 119.1, 110.3, 109.7, 101.4, 101.3, 42.4, 36.5, 35.7, 33.0, 29.9, 27.7, 25.4, 17.4 ppm; HRMS (ESI): m/z: calcd for $C_{34}H_{30}N_4Na^+$: 517.2363, found: 517.2362.

*(E)-6-Bromo-4-(5-bromo-1-methyl-1H-indol-3-yl)-4,9-dimethyl-1-(1-phenylprop-1-en-2-yl)-2,3,4,9-tetrahydro-1H-carbazole (**3p**), isomer1*

IR (neat, ν/cm^{-1}): 3020, 2937, 2856, 1737, 1472, 1362, 1281, 1229, 1147, 1095, 1049, 904, 794, 742; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (s, 1H), 7.44 (s, 1H), 7.31-7.27 (m, 2H), 7.24-7.12 (m, 7H), 6.62 (s, 1H), 6.24 (s, 1H), 3.69 (t, *J* = 5.9 Hz, 1H), 3.66 (s, 3H), 3.65 (s, 3H), 2.47-2.41 (m, 1H), 2.13-2.06 (m, 1H), 1.93-1.84 (m, 2H), 1.90 (s, 3H), 1.87 (s, 3H) ppm; ^{13}C NMR (100 MHz, CD_3Cl): δ = 139.7, 137.8, 137.4, 136.6, 136.2, 128.9, 128.8, 128.0, 127.8, 127.6, 127.4, 126.3, 123.9, 123.5, 123.4, 122.9, 122.6, 118.3, 111.8, 111.7, 110.8, 110.1, 43.5, 36.8, 36.2, 32.8, 29.9, 28.0, 26.1, 16.7 ppm; HRMS (ESI): m/z: calcd for $C_{32}H_{30}Br_2N_2NaO^+$: 623.0668, found: 623.0662.

*(E)-6-Bromo-4-(5-bromo-1-methyl-1H-indol-3-yl)-4,9-dimethyl-1-(1-phenylprop-1-en-2-yl)-2,3,4,9-tetrahydro-1H-carbazole (**3p**), isomer2*

IR (neat, ν/cm^{-1}): 3020, 2937, 2856, 1737, 1472, 1362, 1281, 1229, 1147, 1095, 1049, 904, 794, 742; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (s, 1H), 7.58 (s, 1H), 7.33-7.27 (m, 3H), 7.25-7.22 (m, 6H), 6.28 (s, 1H), 5.84 (s, 1H), 3.61 (s, 3H), 3.58 (s, 3H), 3.58-3.55 (m, 1H), 2.35-2.31 (m, 1H), 2.08-2.04 (m, 1H), 2.03 (s, 3H), 2.01 (s, 3H), 1.83-1.80 (m, 2H) ppm; ^{13}C NMR (100 MHz, CD_3Cl): δ = 138.8, 137.9, 137.5, 136.7, 136.2, 129.8, 128.8, 128.2, 128.1, 127.7, 127.4, 126.3, 123.7, 123.4, 123.3, 123.2, 121.7, 118.1, 111.9, 111.8, 110.9, 110.2, 41.9, 36.3, 34.4, 32.7, 29.4, 29.2, 24.4, 18.0 ppm; HRMS (ESI): m/z: calcd for $C_{32}H_{30}Br_2N_2NaO^+$: 623.0668, found: 623.0662.

*9-Benzyl-4-(1-benzyl-1H-indol-3-yl)-4-methyl-1-(2-methylprop-1-enyl)-2,3,4,9-tetrahydro-1H-carbazole (**3q**)*

Obtained as 1:1 diastereomeric mixture. Characterization of a 1:1 diastereomeric ratio. IR (neat, ν/cm^{-1}): 3060, 3025, 2962, 2928, 2857, 1605, 1463, 1452, 1369, 1326, 1178, 1027, 907, 729, 695; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.31-7.27 (m, 3H), 7.25-7.16 (m, 13H), 7.13-6.96 (m, 11H), 6.94-6.87 (m, 6H), 6.84-6.80 (m, 1H), 6.63 (s, 1H), 5.36-5.15 (m, 10H), 3.72-3.67 (m, 1H), 3.64-3.59 (m, 1H), 2.58 (ddd, *J*= 13.4, 11.1, 2.6 Hz, 1H), 2.48 (ddd, *J* = 13.0, 7.1, 2.4 Hz, 1H), 2.15-2.09 (m, 1H), 2.07 (s, 3H), 2.05-1.96 (m, 1H), 1.95 (s, 3H), 1.92-1.77 (m, 3H), 1.68-1.60 (m, 1H), 1.66 (d, *J* = 1.1 Hz, 3H), 1.63 (d, *J* = 1.1 Hz, 3H), 1.62 (d, *J* = 1.0 Hz, 3H), 1.51 (d, *J* = 1.1 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.7, 138.6, 138.1, 138.0, 137.9, 137.6, 137.5, 137.4, 137.3, 137.2, 131.6, 131.4, 128.7, 128.7, 128.6, 128.5, 128.5, 128.4,

127.6, 127.3, 127.3, 127.2, 126.8, 126.7, 126.6, 126.6, 126.5, 126.4, 126.3, 125.8, 125.7, 124.5, 123.6, 121.2, 121.1, 121.0, 121.0, 120.8, 120.5, 120.5, 120.4, 120.4, 118.5, 118.4, 118.3, 118.3, 117.4, 117.3, 109,8, 109.7, 109.1, 109.0, 49.7, 49.6, 46.3, 46.2, 36.8, 36.2, 36.1, 35.9, 32.4, 32.3, 28.6, 28.2, 28.1, 27.5, 25.6, 25.5, 17.8,17.7 ppm; HRMS (ESI): m/z: calcd for $C_{39}H_{38}N_2Na^+$: 557.2927, found: 557.2924.

*6-Bromo-4-(5-bromo-1-methyl-1H-indol-3-yl)-4,9-dimethyl-1-(2-methylprop-1-enyl)-2,3,4,9-tetrahydro-1H-carbazole (**3r**)*

Obtained as 1:1 diastereomeric mixture. Characterization of a 1:0.45 diastereomeric ratio. IR (neat, v/cm^{-1}): 2962, 2921, 2852, 1471, 1420, 1370, 1275, 1229, 1141, 1089, 1049, 985, 906, 786, 729, 637, 585; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 1.7 Hz, 1H, major isomer), 7.59 (d, *J* = 0.8 Hz, 1H, minor isomer), 7.52 (d, *J* = 1.7 Hz, 1H, major isomer), 7.32 (d, *J* = 1.4 Hz, 1H, minor isomer), 7.27 (d, *J* = 1.8 Hz, 1H, minor isomer), 7.25 (d, *J* = 1.8 Hz, 1H, minor isomer), 7.22 (d, *J* = 1.8 Hz, 1H, minor isomer), 7.20 (d, *J* = 1.8 Hz, 1H, major isomer), 7.16 (s, 1H, major isomer), 7.14-7.11 (m, 2H major isomer and 1H minor isomer), 6.69 (s, 1H, minor isomer), 6.26 (s, 1H, major isomer), 5.37-5.34 (m, 1H, major and minor isomer), 3.81-3.75 (m, 1H, minor isomer), 3.73-3.69 (m, 1H, major isomer), 3.69 (s, 3H, minor isomer), 3.60 (s, 3H, minor isomer), 3.58 (s, 3H, major isomer), 3.57 (s, 3H, major isomer), 2.48-2.42 (m, 1H, minor isomer), 2.35 (ddd, *J* = 13.1, 5.4, 2.3 Hz, 1H, major isomer), 2.10-2.04 (m, 1H, minor isomer), 2.02-1.95 (m, 1H, major isomer), 1.98 (s, 3H, major isomer), 1.85 (s, 3H, minor isomer), 1.83 (d, *J* = 1.1 Hz, 3H, minor isomer), 1.82-1.81 (m, 1H, major isomer), 1.79 (d, *J* = 1.1 Hz, 3H major isomer), 1.77 (bs, 1H, major and minor isomer), 1.74-1.73 (m, 1H, minor isomer), 1.63-1.56 (m, 1H, major and minor isomer) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) (major and minor isomer): δ = 139.7, 139.2, 136.7, 136.6, 136.1, 135.9, 132.0, 131.9, 129.7, 128.4, 128.4, 128.4, 128.3, 127.9, 127.7, 127.6, 127.4, 126.7, 126.6, 123.7, 123.7, 123.4, 123.3, 123.0, 122.9, 122.5, 122.0, 116.0, 115.9, 111.8, 111.6, 110.8, 110.7, 110.0, 36.9, 36.3, 35.7, 35.4, 32.8, 32.7, 32.6, 31.9, 29.7, 29.7, 29.4, 29.0, 27.8, 27.7, 25.8, 25.8, 17.9, 17.9 ppm (two carbon are missing due to overlapping); HRMS (ESI): m/z: calcd for $C_{27}H_{28}Br_2N_2Na^+$: 561.0511, found: 561.0506.

*9-Benzyl-4-(1-benzyl-1H-indol-3-yl)-1-(4-methoxyphenyl)-1,4-dimethyl-2,3,4,9-tetrahydro-1H-carbazole (**3s**)*

Obtained as 1:1 diastereomeric mixture. Characterization of a 1:0.70 diastereomeric ratio. IR (neat, v/cm^{-1}): 3056, 3025, 2963, 2928, 2854, 1606, 1509, 1463, 1350, 1327, 1299, 1245, 1181, 1074, 1029, 908, 828, 730, 696; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 7.8 Hz, 1H, minor isomer), 7.62 (d, *J* = 7.5 Hz, 1H, minor isomer), 7.49 (d, *J* = 7.5 Hz, 1H, major isomer), 7.35-6.83 (m, 21H, major isomer and 17H minor isomer), 6.78 (d, *J* = 6.7 Hz, 2H, minor isomer), 6.70 (s, 1H, major isomer), 6.64 (d, *J* = 8.3 Hz, 2H, minor isomer), 5.38-4.79 (m, 4H, major and minor isomer), 3.82 (s, 3H, major isomer), 3.75 (s, 3H, minor isomer), 2.65-2.53 (m, 1H, major and minor isomer), 2.19 (s, 3H, minor isomer), 2.18-2.13 (m, 1H, minor isomer), 2.06 (s, 3H, major isomer), 2.06-1.99 (m, 1H, major isomer), 1.97-1.89 (m, 1H, major and minor isomer), 1.84-1.79 (m, 1H, major isomer), 1.72-1.68 (m, 1H, minor isomer), 1.67 (s, 3H, major isomer), 1.66 (s, 3H, minor isomer) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) (major and minor isomer): 157.9, 157.7, 141.3, 141.1, 140.7, 140.1, 138.4, 138.3, 138.1, 138.0, 137.7, 137.7, 137.6, 137.5, 128.6, 128.6, 128.4, 128.4, 127.6, 127.6, 127.5, 127.3, 127.3, 127.2, 127.2, 127.1, 126.7, 126.6, 126.5, 126.4, 126.4, 126.2, 126.0, 125.8, 125.7, 124.3, 123.3, 121.4, 121.3, 121.2, 121.1, 120.9, 120.8, 120.7, 118.9, 118.7, 118.6, 118.5, 118.4, 118.3, 113.7, 113.7, 109.9,

109.9, 109.8, 109.8, 55.2, 55.1, 49.7, 49.5, 47.6, 47.5, 42.0, 41.8, 40.1, 40.0, 37.4, 36.3, 36.0, 36.0, 29.7, 29.3, 27.9, 25.7 ppm; HRMS (ESI): m/z: calcd for $C_{43}H_{40}N_2NaO^+$: 623.3033, found: 623.3032.

*1-(4-Methoxyphenyl)-1,4,9-trimethyl-4-(1-methyl-1H-indol-3-yl)-2,3,4,9-tetrahydro-1H-carbazole (**3t**)*

Obtained as 2:1 diastereomeric mixture. Characterization of a 1.5:1 diastereomeric ratio. IR (neat, v/cm^{-1}): 3051, 2963, 2930, 2837, 2358, 1744, 1608, 1509, 1468, 1371, 1326 1247, 1180, 1094, 1032, 908, 828; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 8.0 Hz, 1H, minor isomer), 7.55 (d, *J* = 8.0 Hz, 1H, minor isomer), 7.53-7.51 (m, 1H, major isomer), 7.37 (d, *J* = 7.9 Hz, major isomer), 7.28-7.25 (m, XH), 7.21-7.05 (m, xH), 7.02-6.95 (m, 2H), 6.93-6.89 (m, 1H), 6.84 (d, *J* = 8.8 Hz, 2H, major isomer), 6.78 (d, *J* = 8.8 Hz, 2H, minor isomer), 6.62 (s, 1H, major isomer), 6.52 (s, 1H, minor isomer), 3.81 (s, 3H, major isomer), 3.77 (s, 3H, minor isomer), 3.67 (s, 3H, major isomer), 3.62 (s, 3H, minor isomer), 3.36 (s, 3H, major isomer), 3.24 (s, 3H, minor isomer), 2.59-2.54 (m, 1H, major isomer), 2.43-2.37 (m, 1H, major isomer), 2.14-2.07 (m, 1H, minor isomer), 2.09 (s, 3H, minor isomer), 2.03 (s, 3H, major isomer), 1.95-1.65 (m, 1H major isomer and 3H minor isomer), 1.86 (s, 3H, major isomer), 1.85 (s, 3H, minor isomer) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2) (major and minor isomer): δ = 157.8, 157.6, 141.4, 141.1, 140.5, 140.3, 138.1, 137.9, 137.8, 137.7, 128.8, 127.9, 127.6, 127.2, 127.2, 126.1, 126.0, 126.0, 125.7, 122.9, 122.6, 121.4, 121.1, 121.0, 120.9, 120.8, 120.8, 120.5, 118.4, 118.4, 118.3, 118.1, 118.1, 117.8, 113.7, 113.6, 109.3, 109.2, 108.5, 108.4, 55.2, 55.1, 41.6, 41.2, 39.9, 37.1, 36.5, 36.1, 35.8, 32.5, 32.5, 31.6, 31.1, 29.4, 28.7, 28.7, 28.7, 25.1 ppm; HRMS (ESI): m/z: calcd for $C_{31}H_{32}N_2NaO^+$: 471.2406, found: 471.2409.

*6-Bromo-4-(5-bromo-1H-indol-3-yl)-1-(4-methoxyphenyl)-4-methyl-2,3,4,9-tetrahydro-1H-carbazole (**3u**)*

Obtained as 1:1 diastereomeric mixture. Characterization of a 1:0.76 ratio of diastereoisomers. IR (neat, v/cm^{-1}): 3420, 2962, 2933, 2852, 1605, 1507, 1455, 1310, 1235, 1170, 1025, 910, 800, 730; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (bs, 1H, minor isomer), 7.91 (s, 1H, major isomer), 7.88 (bs, 1H, major isomer), 7.56 (d, *J* = 1.3 Hz, 1H, major isomer), 7.54 (d, *J* = 7.5 Hz, 2H, minor isomer), 7.41 (s, 1H, minor isomer), 7.28-7.04 (m, 7H major isomer, 9H minor isomer) , 6.98 (d, *J* = 2.0 Hz, 1H, minor isomer), 6.91 (d, *J* = 8.6 Hz, 2H, minor isomer), 6.86 (d, *J* = 8.6 Hz, 2H, major isomer), 6.62 (d, *J* = 2.3 Hz, 1H, major isomer), 4.22 (dd, *J* = 8.0, 5.7 Hz, 1H, minor isomer), 4.08 (dd, *J* = 10.2, 5.5 Hz, 1H, major isomer), 3.83 (s, 3H, minor isomer), 3.79 (s, 3H, major isomer), 2.61-2.57 (m, 1H, major isomer), 2.46-2.39 (m, 1H, minor isomer), 2.20-2.13 (m, 1H, major isomer), 2.06-1.94 (m, 1H major isomer, 3H minor isomer), 2.02 (s, 3H, major isomer), 1.96 (s, 3H, minor isomer), 177-1.68 (m, 1H, major isomer) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.7, 158.6, 138.0, 137.0, 136.0, 135.9, 135.4, 135.3, 134.7, 134.7, 129.3, 129.1, 128.5, 128.3, 127.5, 127.1, 124.9, 124.4, 124.4, 124.4, 123.9, 123.8, 123.8, 123.4, 123.1, 123.1, 123.0, 122.4, 118.0, 117.9, 114.3, 114.2, 112.8, 112.7, 112.3, 112.3, 112.2, 112.1, 112.0, 55.3, 55.3, 41.5, 40.7, 38.5, 37.7, 36.4, 35.4, 30.7, 30.4, 28.7, 27.5 ppm (one carbon missing due to overlapping); HRMS (ESI): m/z: calcd for $C_{28}H_{24}Br_2N_2NaO^+$: 585.0147, found: 585.0140.

*6-Bromo-1-(5-bromo-1H-indol-3-yl)-4-(4-methoxyphenyl)-1-methyl-2,3,4,9-tetrahydro-1H-carbazole (**3'u**)*

Obtained as 1:1 diastereomeric mixture. Characterization of a 1:1 ratio of diastereoisomers. IR (neat, v/cm^{-1}): 3425, 2933, 2846, 1605, 1508, 1461, 1298, 1240, 1175, 1106, 1031, 905, 795, 727, 581; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (bs, 2H), 7.83 (s, 1H), 7.71 (s, 1H), 7.65 (s, 1H), 7.28 (s, 1H), 7.25-7.21 (m, 4H), 7.19-7.10 (m, 8H), 7.05-7.01 (m, 2H), 6.91 (d, *J* = 2.3 Hz, 1H), 6.87-6.85 (m, 5H), 4.26 (t, *J* = 6.5 Hz, 1H), 4.20 (t, *J* = 6.0 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 2.50-2.45 (m, 1H), 2.43-2.36 (m, 1H), 2.30-2.23 (m, 1H), 2.20-2.14 (m, 1H), 1.94-1.80 (m, 4H), 1.91 (s, 3H), 1.87 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.0, 157.9, 142.6, 142.4, 137.6, 137.3, 135.7, 135.6, 134.6, 134.5, 129.2, 128.9, 128.9, 127.0, 126.8, 125.0, 124.9, 124.2, 124.0, 123.8, 123.3, 123.1, 122.9, 122.8, 122.7, 122.3, 122.2, 113.9, 113.8, 112.8, 112.8, 112.7, 112.7, 112.4, 112.3, 112.1, 112.0, 111.7, 111.6, 55.2, 55.2, 38.9, 38.4, 36.5, 36.1, 36.0, 35.7, 31.6, 31.0, 27.6, 27.4 ppm (one carbon missing due to overlapping); HRMS (ESI): m/z: calcd for $C_{28}H_{24}Br_2N_2NaO^+$: 585.0147, found: 585.0139.

*1-(4-Methoxyphenyl)-4,6-dimethyl-4-(5-methyl-1H-indol-3-yl)-2,3,4,9-tetrahydro-1H-carbazole (**3v**)*

Obtained as 1:1 diastereomeric mixture. Characterization of a 1:0.78 ratio of diastereoisomers. IR (neat, v/cm^{-1}): 3408, 2962, 2927, 2857, 1507, 1460, 1298, 1240, 1164, 1031, 921, 806, 732, 419; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (bs, 1H, minor isomer), 7.71 (bs, 1H, major isomer), 7.68 (s, 1H, major isomer), 7.43 (s, 1H, minor isomer), 7.36 (s, 1H major, 1H minor), 7.31 (s, 1H, major isomer), 7.24 (s, 1H, major isomer), 7.22 (s, 1H, minor isomer), 7.13-7.08 (m, 3H major isomer and 4H minor isomer), 7.03-6.82 (m, 4H major isomer and 3H minor isomer), 6.75 (d, *J* = 1.7 Hz, 1H, minor isomer), 6.57 (d, *J* = 2.2 Hz, 1H, major isomer), 4.18 (t, *J* = 6.0 Hz, 1H, minor isomer), 4.07 (dd, *J* = 10.6, 5.6 Hz, 1H, major isomer), 3.82 (s, 3H, minor isomer), 3.79 (s, 3H, major isomer), 2.70-2.66 (m, 1H, major isomer), 2.50 (s, 3H, major isomer), 2.46-2.42 (m, 1H, minor isomer), 2.39 (s, 3H, minor isomer), 2.34 (s, 3H, major isomer), 2.29 (s, 3H, minor isomer), 2.18-2.08 (m, 1H, major isomer), 2.10 (s, 3H, major isomer), 2.05 (s, 3H, minor isomer), 2.04-1-86 (m, 1H major and 3H minor), 1.78-1.69 (m, 1H, major isomer) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.5, 158.4, 136.7, 136.2, 136.1, 135.8, 135.6, 135.4, 134.5, 134.5, 129.3, 129.2, 129.0, 128.2, 127.9, 127.9, 127.7, 127.7, 127.1, 127.0, 126.0, 125.6, 124.6, 124.1, 123.7, 122.9, 122.4, 122.3, 120.8, 120.7, 120.6, 120.5, 118.6, 118.1, 114.0, 113.9, 111.0, 110.8, 110.2, 110.1, 55.3, 55.2, 41.8, 40.2, 38.5, 36.7, 36.6, 35.9, 30.7, 30.5, 29.7, 28.7, 27.9, 21.7, 21.5, 21.5 ppm; HRMS (ESI): m/z: calcd for $C_{30}H_{30}N_2NaO^+$: 457.2250, found: 457.2252.

*4-(4-Methoxyphenyl)-1,6-dimethyl-1-(5-methyl-1H-indol-3-yl)-2,3,4,9-tetrahydro-1H-carbazole (**3'v**)*

Obtained as 1:1 diastereomeric mixture. Characterization of a 1:0.57 ratio of diastereoisomers. IR (neat, v/cm^{-1}): 3405, 2927, 2846, 1611, 1509, 1460, 1300, 1243, 1174, 1031, 908, 795, 732; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (bs, 2H major and minor isomer), 7.72 (s, 1H, minor isomer), 7.62 (s, 1H, major isomer), 7.34 (s, 1H, minor isomer), 7.25-7.21(m, 1H major isomer and 2H minor isomer), 7.19 (d, *J* = 8.5 Hz, 2H, major isomer), 7.14 (d, *J* = 8.2 Hz, 1H, minor isomer), 7.08 (d, *J* = 8.2 Hz, 1H, major isomer), 7.05 (s, 1H, major isomer), 7.00-6.95 (m, 1H, minor isomer), 6.97 (dd, *J* = 8.3, 1.2 Hz, 1H major), 6.91 (dd, *J* = 8.2, 1.2 Hz, 1H, minor isomer) 6.88 (s, 1H, minor isomer), 6.78 (s, 1H, minor isomer), 6.88-6.82 (m, 3H major isomer and 5H minor isomer), 6.69 (s, 1H, major isomer), 4.28 (t, *J* = 6.3 Hz, 1H, major isomer), 4.23 (t, *J* = 6.0 Hz, 1H, minor isomer), 3.82 (s, 3H, major isomer), 3.79 (s,

3H, minor isomer), 2.59-2.53 (m, 1H, minor isomer), 2.50-2.45 (m, 1H major isomer and minor isomer), 2.36 (s, 3H, minor isomer), 2.30 (s, 3H, major isomer), 2.29 (s, 3H, minor isomer), 2.27 (s, 3H, major isomer), 2.22-2.14 (m, 1H major and minor isomer), 1.94-1.83 (m, 2H major isomer, 1H minor isomer), 1.92 (s, 3H, major isomer), 1.88 (s, 3H, minor isomer) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.7, 157.6, 142.1, 141.8, 138.5, 138.2, 135.4, 135.3, 134.2, 134.1, 129.1, 129.0, 128.5, 128.3, 128.2, 127.9, 127.7, 127.4, 125.6, 125.4, 123.5, 123.4, 122.9, 122.8, 122.7, 122.6, 122.5, 122.4, 120.5, 120.2, 119.4, 119.4, 113.5, 113.5, 111.0, 110.9, 110.9, 110.8, 110.3, 110.2, 55.2, 55.2, 39.1, 38.5, 36.2, 36.1, 35.9, 35.8, 31.8, 31.1, 27.9, 27.5, 21.7, 21.5, 21.4, 21.4 ppm; HRMS (ESI): m/z: calcd for $C_{30}H_{30}N_2NaO^+$: 457.2250, found: 457.2249.

*5-(5-Cyano-1H-indol-3-yl)-8-(4-methoxyphenyl)-5-methyl-6,7,8,9-tetrahydro-5H-carbazole-3-carbonitrile (**3w**)*

Obtained as 1:1 diastereomeric mixture. IR (neat, ν/cm^{-1}): 3316, 2927, 2852, 2218, 1613, 1509, 1469, 1339, 1310, 1245, 1177, 1033, 908, 807, 731, 647; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63 (s, 1H), 8.49 (s, 1H), 8.09 (s, 1H), 8.05 (s, 1H), 7.97 (s, 1H), 7.73 (s, 1H), 7.49-7.34 (m, 8H), 7.31 (s, 1H), 7.28 (d, *J* = 5.4 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 6.87 (s, 1H), 4.36 (dd, *J* = 10.1, 5.6 Hz, 1H), 4.20 (dd, *J* = 8.7, 5.8 Hz, 1H), 3.89 (s, 3H), 3.83 (s, 3H), 2.61-2.58 (m, 1H), 2.55-2.50 (m, 1H), 2.33-2.30 (m, 1H), 2.23-2.16 (m, 2H), 2.10-2.00 (m, 2H), 2.06 (s, 3H), 2.00 (s, 3H), 1.85 (dd, *J* = 22.2, 10.1 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.8, 158.7, 139.0, 138.8, 138.3, 137.8, 137.6, 134.6, 134.5, 129.3, 129.0, 129.0, 128.2, 126.4, 126.3, 126.1, 125.8, 125.7, 125.6, 125.4, 125.1, 125.0, 124.9, 124.7, 124.6, 124.5, 124.3, 124.2, 123.1, 121.0, 120.9, 120.9, 118.5, 118.4, 114.4, 114.3, 112.4, 112.3, 111.6, 111.5, 102.0, 102.0, 101.8, 101.6, 55.3, 55.3, 41.2, 40.7, 39.0, 38.1, 36.1, 34.9, 31.0, 30.0, 28.6, 27.2, ppm; HRMS (ESI): m/z: calcd for $C_{30}H_{24}N_4NaO^+$: 479.1842, found: 479.1845.

*8-(5-Cyano-1H-indol-3-yl)-5-(4-methoxyphenyl)-8-methyl-6,7,8,9-tetrahydro-5H-carbazole-3-carbonitrile (**3'w**)*

Obtained as 1:1 diastereomeric mixture. Characterization of a 1:0.79 ratio of diastereoisomers. IR (neat, ν/cm^{-1}): 3321, 2926, 2857, 2218, 1614, 1509, 1471, 1244, 1176, 1031, 907, 806, 730; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.48 (s, 1H, minor isomer), 8.42 (s, 1H, major isomer), 8.19 (s, 1H, major isomer), 7.91 (s, 1H major and minor), 7.43-7.24 (m, 4H major isomer and 6H minor isomer), 7.21 (d, *J* = 2.1 Hz, 1H, minor isomer), 7.17-7.15 (m, 3H, major isomer), 7.12 (d, *J* = 8.5 Hz, 2H, major isomer), 6.94 (d, *J* = 2.2 Hz, 1H, major isomer), 6.89-6.86 (m, 4H, minor isomer), 4.32 (dd, *J* = 8.4, 5.9 Hz, 1H, minor isomer), 4.23 (t, *J* = 6.52, 1H, major isomer), 3.84 (s, 3H, minor isomer), 3.80 (s, 3H, major isomer), 2.51-2.41 (m, 2H, major isomer), 2.30-2.19 (m, 2H, major isomer), 2.04-1.93 (m, 2H, minor isomer), 1.95 (s, 3H, minor isomer), 1.92 (s, 3H, major isomer), 1.87-1.79 (m, 2H, minor isomer) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.3, 158.2, 143.0, 142.9, 141.6, 141.5, 141.3, 138.8, 138.7, 137.7, 137.6, 136.9, 136.5, 128.8, 128.7, 127.2, 126.8, 126.1, 125.7, 125.6, 125.3, 125.2, 125.1, 124.9, 124.8, 124.7, 124.6, 124.1, 123.9, 123.7, 120.9, 120.8, 120.4, 114.1, 113.3, 113.2, 112.4, 112.3, 111.5, 111.3, 102.9, 102.7, 102.4, 102.2, 55.2, 39.6, 38.5, 37.6, 36.4, 36.2, 35.5, 31.9, 30.9, 27.4, 27.4 ppm; HRMS (ESI): m/z: calcd for $C_{30}H_{24}N_4NaO^+$: 479.1842, found: 479.1840.

Analytical data for representative vinyl-cyclopropyl indoles

*3-(1-(2-(4-Methoxyphenyl)cyclopropyl)vinyl)-1-methyl-1H-indole (**5b**)*

IR (neat, ν/cm^{-1}): 3043, 3008, 2927, 2834, 1612, 1512, 1472, 1464, 1244, 1225, 1177, 1103, 1034, 833, 806, 737, 539; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.92 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.18-7.12 (m, 4H), 6.89 (d, *J* = 8.6 Hz, 2H), 5.47 (s, 3H), 5.08 (s, 3H), 3.81 (s, 3H), 3.72 (s, 3H), 2.07-1.97 (m, 2H), 1.47-1.42 (m, 1H), 1.21 (td, *J* = 8.6, 5.3 Hz, 1H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 158.5, 143.2, 138.2, 135.5, 128.5, 127.2, 126.5, 122.3, 121.2, 120.3, 117.0, 114.4, 110.0, 106.2, 55.8, 33.3, 29.3, 25.6, 15.5 ppm; HRMS (ESI): m/z: calcd for $C_{21}H_{22}NO^{+}$: 304.1696, found: 304.1694.

*Experimental procedure for allene **6***

TFA (0.186 mmol, 80 mol%) was added to a solution of indole (0.232 mmol, 1.0 eq.) and cyclopropyl alkyne (0.232 mmol, 1.0 eq.) in dry toluene (0.1 M). The mixture was heated up to 80 ^{o}C and stirred until consumption of the starting materials. Then, water was added and extracted with DCM. The combined organic layers were dried over anhydrous $MgSO_4$ and the solvent was evaporated under vacuum. The residue was purified by flash chromatography (Hexane:EtOAc).

*1-Benzyl-3-(1-(4-methoxyphenyl)penta-3,4-dienyl)-1H-indole (**6a**)*

IR (neat, ν/cm^{-1}): 3048, 2991, 2927, 2898, 2834, 1947, 1609, 1509, 1482, 1466, 1327, 1244, 1175, 1034, 841, 738, 550; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (d, *J* = 7.9 Hz, 1H), 7.27-7.23 (m, 3H), 7.21-7.16 (m, 3H), 7.09-7.05 (m, 3H), 6.98-6.93 (m, 2H), 6.77 (d, *J* = 8.6 Hz, 2H), 5.24 (s, 2H), 5.03 (q, *J* = 7.0 Hz, 1H), 4.52-4.49 (m, 2H), 4.23 (t, *J* = 7.5 Hz, 1H), 3.72 (s, 3H), 2.86-2.78 (m, 1H), 2.69-2.61 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.0, 157.9, 137.8, 136.9, 136.7, 128.9, 128.7, 127.7, 127.5, 126.6, 125.5, 121.7, 119.7, 118.9, 118.9, 113.6, 109.5, 88.6, 74.4, 55.2, 49.9, 42.2, 35.5 ppm; HRMS (ESI): m/z: calcd for $C_{27}H_{25}NNaO^{+}$: 402.1828, found: 402.1823.

*3-(1-(4-Methoxyphenyl)penta-3,4-dienyl)-1-methyl-1H-indole (**6b**)*

IR (neat, ν/cm^{-1}): 3048, 2991, 2927, 2898, 2834, 1947, 1609, 1509, 1482, 1466, 1327, 1244, 1175, 1034, 841, 738, 550; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.38 (d, J = 7.9 Hz, 1H), 7.28 (d, J = 8.2 Hz, 1H), 7.22 (d, J = 8.6 Hz, 2H), 7.15 (t, J = 7.6 Hz, 1H), 6.97 (t, J = 7.4 Hz, 1H), 6.93 (s, 1H), 6.82 (d, J = 8.6 Hz, 2H), 5.09 (q, J = 7.0 Hz, 1H), 4.66-4.56 (m, 1H), 4.24 (t, J = 7.6 Hz, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 2.91-2.83 (m, 1H), 2.74-2.66 (m, 1H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 209.6, 158.6, 137.8, 137.6, 129.4, 127.9, 126.6, 122.000, 119.8, 119.1, 118.7, 114.1, 109.7, 89.1, 74.7, 55.7, 42.7, 35.9, 33.1 ppm; HRMS (ESI): m/z: calcd for $C_{21}H_{21}NNaO^{+}$: 326.1515, found: 326.1512.

*9-Benzyl-4-(4-methoxyphenyl)-1-methyl-4,9-dihydro-3H-carbazole (**7'a**)*

IR (neat, ν/cm^{-1}): 3060, 3025, 2933, 2829, 1608, 1508, 1463, 1452, 1353, 1300, 1245, 1176, 1033, 830, 740; ^{1}H NMR (400 MHz, Toluene-*d*^{8}): δ = 7.19 (d, *J* = 8.6 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.04-6.94 (m, 5H), 6.80 (d, *J* = 7.0 Hz, 2H), 6.73 (d, *J* = 8.6 Hz, 2H), 5.44-5.41 (m, 1H), 5.13 (s, 2H), 4.27-4.22 (m, 1H), 3.33 (s, 3H), 2.68-2.48 (m, 2H), 1.91 (d, *J* = 1.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Toluene-*d*^{8}): δ = 158.8, 139.2, 138.9, 136.4, 129.2, 127.4, 127.2, 126.8, 125.7, 122.1, 120.3, 120.2, 114.1, 109.7, 54.6, 48.2, 38.9, 35.1 ppm; MS (ESI): m/z [M+1]$^{+}$ = 380.2.

*1-(4-Methoxyphenyl)-4,9-dimethyl-2,9-dihydro-1H-carbazole (**7b**)*

IR (neat, ν/cm^{-1}): 3051, 2999, 2929, 2858, 2837, 1609, 1508, 1461, 1451, 1365, 1301, 1240, 1175, 1033, 829, 738, 549; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.29 (d, *J* = 8.3 Hz, 1H), 7.17-7.15 (m, 2H), 7.10 (ddd, *J* = 8.2, 6.6, 1.5 Hz, 1H), 6.94-6.87 (m, 1H), 6.81-6.79 (m, 2H), 5.68 (dt, *J* = 4.8, 1.6 Hz, 1H), 4.22 (t, *J* = 8.0 Hz, 1H), 3.92 (s, 3H), 3.77 (s, 3H), 7.79-7.71 (m, 1H), 2.57-2.49 (m, 1H), 2.32 (d, *J* = 1.7 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 158.8, 138.8, 137.7, 137.2, 129.3, 129.3, 127.9, 126.3, 124.7, 121.6, 119.7, 119.4, 114.1, 109.6, 55.7, 38.3, 34.9, 32.6, 21.2 ppm; HRMS (ESI): m/z: calcd for $C_{21}H_{21}NNaO^{+}$: 326.1515, found: 326.1512.

*4-(4-Methoxyphenyl)-9-methyl-1-methylene-2,3,4,9-tetrahydro-1H-carbazole (**7'b**)*

IR (neat, ν/cm^{-1}): 3056, 2999, 2932, 2832, 1723, 1609, 1508, 1464, 1367, 1240, 1174, 1035, 830, 744, 710, 554; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.31 (d, *J* = 8.3 Hz, 1H), 7.17-7.13 (m, 1H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.87-6.84 (m, 2H), 6.82-6.79 (m, 2H), 5.38 (s, 1H), 5.16 (s, 1H), 4.32 (t, *J* = 6.4 Hz, 1H), 3.91 (s, 3H), 3.77 (s, 3H), 2.66-2.59 (m, 1H), 2.37-2.29 (m, 1H), 1.96-1.88 (s, 1H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 158.7, 139.8, 138.7, 138.6, 135.6, 129.5, 126.6, 122.9, 120.5, 119.4, 116.8, 114.1, 109.6, 108.6, 55.7, 40.2, 36.2, 33.6, 32.8 ppm; HRMS (ESI): m/z: calcd for $C_{21}H_{21}NNaO^{+}$: 326.1515, found: 326.1513.

*9-Benzyl-1-(4-methoxyphenyl)-4-methyl-4-(1-methyl-1H-indol-3-yl)-2,3,4,9-tetrahydro-1H-carbazole (**9**)*

Obtained as 1:1 diastereomeric mixture. Characterization of a 1:0.70 diastereomeric ratio. IR (neat, ν/cm^{-1}): 3046, 2926, 2858, 1603, 1509, 1462, 1453, 1374, 1327, 1244, 1176, 1031, 908, 832, 806, 734, 699, 561; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 8.0 Hz, 1H, minor isomer), 7.66 (d, *J* = 8.0 Hz, 1H, major isomer), 7.54 (d, *J* = 7.9 Hz, 1H, major isomer), 7.46 (d, *J* = 7.9 Hz, 1H, minor isomer), 7.30-6.75 (m, 15H major isomer and 16 H minor isomer), 6.44 (s, 1H, major isomer), 5.17-5.13 (m, 1H, major and minor isomer), 4.80-4.76 (m, 1H, major and minor isomer), 4.02 (dd, *J* = 5.5, 2.7 Hz, 1H, major isomer), 3.99 (t, *J* = 5.8 Hz, 1H, minor isomer), 3.81 (s, 3H, major isomer), 3.76 (s, 3H, minor isomer), 3.71 (s, 3H, minor isomer), 3.64 (s, 3H, major isomer), 2.41-2.36 (m, 1H, minor isomer), 2.34-2.30 (m, 1H, major isomer), 2.27-2.21 (m, 1H, minor isomer), 2.14 (s, 3H, major isomer), 2.11-2.05 (m, 1H, major isomer), 2.03 (s, 3H, minor isomer), 2.00-1.95 (m, 1H, minor isomer), 1.94-1.89 (m, 1H, major isomer), 1.81-1.76 (m, 1H, minor isomer), 1.68-1.64 (m, 1H, major isomer) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) (major and minor isomer): δ = 158.1, 158.1, 138.4, 138.3,

137.9, 137.8, 137.4, 137.4, 136.5, 136.4, 136.2, 136.0, 129.1, 128.8, 128.6, 128.6, 128.5, 128.3, 127.8, 127.7, 127.1, 126.9, 126.5, 126.4, 126.3, 126.3, 126.1, 126.0, 125.9, 123.3, 122.5, 121.3, 121.1, 120.8, 120.8, 120.7, 119.6, 119.3, 118.6, 118.5, 118.1, 118.0, 113.8, 113.8, 109.3, 109.3, 109.2, 109.2, 55.2, 55.2, 46.5, 46.3, 37.9, 36.7, 36.5, 36.4, 34.5, 32.6, 32.6, 31.1, 30.1, 29.7, 29.2, 28.2 ppm (one carbon is missing due to overlapping); HRMS (ESI): m/z: calcd for $C_{36}H_{34}N_2NaO^+$: 533.2563, found: 533.2563.

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References

[1] J. R. Andreatta,B. A. McKeown,T. B. Gunnoe, 'Transition metal catalyzed hydroarylation of olefins using unactivated substrates: Recent developments and challenges', *J. Organomet. Chem.* **2011**, *696*, 305-315.

[2] T. de Haro,C. Nevado, '*Hydroarylation Reactions* ', Elsevier, Amsterdam, 2014,Vol. 5, p 1621-1659.

[3] C. Nevado,A. M. Echavarren, 'Transition metal-catalyzed hydroarylation of alkynes', *Synthesis* **2005**, 167-182; T. Kitamura, 'Transition-Metal-Catalyzed Hydroarylation Reactions of Alkynes Through Direct Functionalization of C-H Bonds: A Convenient Tool for Organic Synthesis', *Eur. J. Org. Chem.* **2009**, 1111-1125; P. de Mendoza,A. M. Echavarren, 'Synthesis of arenes and heteroarenes by hydroarylation reactions catalyzed by electrophilic metal complexes', *Pure Appl. Chem.* **2010**, *82*, 801-820; Y. Yamamoto, 'Synthesis of heterocycles via transition-metal-catalyzed hydroarylation of alkynes', *Chem. Soc. Rev.* **2014**, *43*, 1575-1600.

[4] A. S. K. Hashmi,G. J. Hutchings, 'Gold catalysis', *Angew. Chem. Int. Ed.* **2006**, *45*, 7896-7936; A. M. Echavarren,C. Nevado, 'Non-stabilized transition metal carbenes as intermediates in intramolecular reactions of alkynes with alkenes', *Chem. Soc. Rev.* **2004**, *33*, 431-436; E. Jimenez-Nunez,A. M. Echavarren, 'Molecular diversity through gold catalysis with alkynes', *Chem. Commun.* **2007**, 333-346; D. J. Gorin,F. D. Toste, 'Relativistic effects in homogeneous gold catalysis', *Nature* **2007**, *446*, 395-403; M. T. Reetz,K. Sommer, 'Gold-catalyzed hydroarylation of alkynes', *Eur. J. Org. Chem.* **2003**, 3485-3496; Z. J. Shi,C. He, 'Efficient functionalization of aromatic C-H bonds catalyzed by gold(III) under mild and solvent-free conditions', *J. Org. Chem.* **2004**, *69*, 3669-3671; A. S. K. Hashmi,M. Rudolph,J. P. Weyrauch,M. Woelfle,W. Frey,J. W. Bats, 'Gold catalysis: Proof of arene oxides as intermediates in the phenol synthesis', *Angew. Chem. Int. Ed.* **2005**, *44*, 2798-2801; A. S. K. Hashmi,L. Grundl, 'Gold catalysis: five new bonds by a domino hydroarylation/cycloisomerization', *Tetrahedron* **2005**, *61*, 6231-6236; C. Nevado,A. M. Echavarren, 'Intramolecular hydroarylation of alkynes catalyzed by platinum or gold: Mechanism and endo selectivity', *Chem. Eur. J.* **2005**, *11*, 3155-3164; A. S. K. Hashmi,L. Schwarz,J. H. Choi,T. M. Frost, 'A new gold-catalyzed C-C bond formation', *Angew. Chem. Int. Ed.* **2000**, *39*, 2285-2288.

[5] C. Ferrer,C. H. M. Amijs,A. M. Echavarren, 'Intra- and intermolecular reactions of indoles with alkynes catalyzed by gold', *Chem. Eur. J.* **2007**, *13*, 1358-1373.

[6] Z. G. Li,Z. J. Shi,C. He, 'Addition of heterocycles to electron deficient olefins and alkynes catalyzed by gold(III)', *J. Organomet. Chem.* **2005**, *690*, 5049-5054.

[7] M. P. Munoz,M. C. de la Torre,M. A. Sierra, 'Platinum-Catalysed Bisindolylation of Allenes: A Complementary Alternative to Gold Catalysis', *Chem. Eur. J.* **2012**, *18*, 4499-4504.

[8] M. Z. Wang,C. Y. Zhou,C. M. Che, 'A silver-promoted auto-tandem catalysis for the synthesis of multiply substituted tetrahydrocarbazoles', *Chem. Commun.* **2011**, *47*, 1312-1314.

[9] V. Pirovano,L. Decataldo,E. Rossi,R. Vicente, 'Gold-catalyzed synthesis of tetrahydrocarbazole derivatives through an intermolecular cycloaddition of vinyl indoles and N-allenamides', *Chem. Commun.* **2013**, *49*, 3594-3596.

[10] V. Pirovano,M. Dell'Acqua,D. Facoetti,D. Nava,S. Rizzato,G. Abbiati,E. Rossi, 'Cycloaddition versus Alkylation Reactions of 2-Vinylindoles with alpha,beta-Unsaturated Carbonyl Compounds Under Gold Catalysis', *Eur. J. Org. Chem.* **2013**, *358*, 6267-6279.

[11] V. Pirovano,E. Arpini,M. Dell'Acqua,R. Vicente,G. Abbiati,E. Rossi, 'Gold(I)-Catalyzed Synthesis of Tetrahydrocarbazoles via Cascade [3,3]-Propargylic Rearrangement/[4+2] Cycloaddition of Vinylindoles and Propargylic Esters', *Adv. Synth. Catal.* **2016**, *358*, 403-409.

[12] J. Bonjoch,D. Sole, 'Synthesis of strychnine', *Chem. Rev.* **2000**, *100*, 3455-3482.

[13] D. Garayalde,K. Kruger,C. Nevado, 'Gold-Catalyzed Cyclopenta- and Cycloheptannulation Cascades: A Stereocontrolled Approach to the Scaffold of Frondosins A and B', *Angew. Chem. Int. Ed.* **2011**, *50*, 911-915.

[14] G. A. Olah,G. K. S. Prakash,T. Nakajima, 'Two- and Threefold Degenerate Rearrangements in Dimethylcyclopropylcarbinyl and Trimethylcyclopropylcarbinyl Cations', *J. Am. Chem. Soc.* **1982**, *104*, 1031-1033; G. A. Olah,V. P. Reddy,G. K. S. Prakash, 'Long-Lived Cyclopropylcarbinyl Cations', *Chem. Rev.* **1992**, *92*, 69-95; G. A. Olah,G. K. S. Prakash,G. Rasul, 'Ab initio/GIAO-CCSD(T) study of structures, energies, and C-13 NMR chemical shifts of $C4H7^+$ and $C5H9^+$ ions: Relative stability and dynamic aspects of the cyclopropylcarbinyl vs bicyclobutonium ions', *J. Am. Chem. Soc.* **2008**, *130*, 9168-9172; G. K. S. Prakash, 'Electrophilic intermediates and their reactions in superacids', *J. Org. Chem.* **2006**, *71*, 3661-3676.

[15] Y. Zou,D. Garayalde,Q. R. Wang,C. Nevado,A. Goeke, 'Gold-Catalyzed Cycloisomerization of Cyclopropyl Alkynyl Acetates: A Versatile Approach to 5-, 6-, and 7-Membered Carbocycles', *Angew. Chem. Int. Ed.* **2008**, *47*, 10110-10113; P. Mauleon,J. L. Krinsky,F. D. Toste, 'Mechanistic Studies on Au(I)-Catalyzed [3,3]-Sigmatropic Rearrangements using Cyclopropane Probes', *J. Am. Chem. Soc.* **2009**, *131*, 4513-4520; D. Garayalde,E. Gomez-Bengoa,X. G. Huang,A. Goeke,C. Nevado, 'Mechanistic Insights in Gold-Stabilized Nonclassical Carbocations: Gold-Catalyzed Rearrangement of 3-Cyclopropyl Propargylic Acetates', *J. Am. Chem. Soc.* **2010**, *132*, 4720-4730.

[16] E. Herrero-Gomez,C. Nieto-Oberhuber,S. Lopez,J. Benet-Buchholz,A. M. Echavarren, 'Cationic eta(1)/eta(2)-gold(I) complexes of simple arenes', *Angew. Chem. Int. Ed.* **2006**, *45*, 5455-5459.

[17] T. T. Dang,F. Boeck,L. Hintermann, 'Hidden Bronsted Acid Catalysis: Pathways of Accidental or Deliberate Generation of Triflic Acid from Metal Triflates', *J. Org. Chem.* **2011**, *76*, 9353-9361.

[18] A. S. K. Hashmi, 'Homogeneous Gold Catalysis Beyond Assumptions and Proposals-Characterized Intermediates', *Angew. Chem. Int. Ed.* **2010**, *49*, 5232-5241.

[19] A. S. K. Hashmi,W. B. Yang,F. Rominger,C. Invest, 'Gold(I)-Catalyzed Formation of Benzo[b]furans from 3-Silyloxy-1,5-enynes', *Angew. Chem. Int. Ed.* **2011**, *50*, 5761-5764; A. S. K.

Hashmi,W. B. Yang,F. Rominger, 'Gold-Catalysis: Highly Efficient and Regio-Selective Carbonyl Migration in Alkynyl-Substituted Indole-3-Carboxamides Leading to Azepino[3,4-b]indol-1-ones', *Adv. Synth. Catal.* **2012**, *354*, 1273-1279.